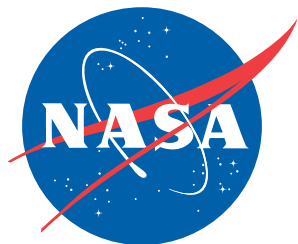


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NESC-RP-08-115/08-00474



Review of Alpha-Ketoglutaric Acid (AKGA) Hydrazine and Monomethylhydrazine (MMH) Neutralizing Compound

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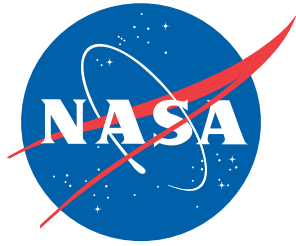
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August 2009

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Review of Alpha-Ketoglutaric Acid (AKGA) Hydrazine and Monomethylhydrazine (MMH) Neutralizing Compound

November 14, 2008

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Report Approval and Revision History

NOTE: This document was approved at the November 14, 2008, NRB. This document was submitted to the NESC Director on December 9, 2008, for configuration control.

Approved:	Original signature on file - RR	12-9-08
1.0	NESC Director	Date

Revision	Description of Revision	Author	Effective Date
1.0	Initial Release	NESC Principal Engineer's Office (Back-up), Andreas W. Dibbern, KSC	11-14-08


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Volume I: Technical Assessment Report

1.0 Notification and Authorization

Mr. William Gerstenmaier, National Aeronautics and Space Administration (NASA) Associate Administrator for the Space Operations Mission Directorate (SOMD) at NASA Headquarters, requested the Johnson Space Center (JSC) White Sands Test Facility (WSTF) and the NASA Engineering and Safety Center (NESC) to evaluate a process for the treatment of hydrazine and monomethylhydrazine (MMH)-contaminated hardware using alpha-ketoglutaric acid (AKGA). This evaluation was prompted by preliminary testing at the Kennedy Space Center (KSC) indicating initial positive results and suggesting cost and operational benefits to NASA.

Dr. Harold Beeson (WSTF Laboratories Office Chief) and Mr. Andreas Dibbern (NESC Principal Engineer's Office) were chosen as team leads and followed NESC guidelines for the development of a position paper. The NESC out-of-board activity was approved June 19, 2008. The final report was presented to the NESC Review Board (NRB) on November 14, 2008.


The key stakeholder for this assessment is Mr. William Gerstenmaier. The project's point of contact is Mr. Chuck Davis, Propellant Lead at KSC.

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2.0 Signature Page


Team signature on file

<hr/> Mr. Andreas W. Dibbern	<hr/> Date	<hr/> Dr. Harold D. Beeson	<hr/> Date
<hr/> Dr. Benjamin Greene	<hr/> Date	<hr/> Dr. Thomas J. Giordano	<hr/> Date

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3.0 Team List

Name	Discipline	Organization/Location
Core Team		
Dr. Harold D. Beeson	WSTF Lead	JSC WSTF
Mr. Andreas W. Dibbern	NESC Lead	NESC/KSC
Dr. Benjamin Greene	Chemistry	JSC WSTF/NTEC
Dr. Thomas J. Giordano	Chemistry	CH2M HILL
Mr. Chris Johansen	MTSO Program Analyst	NESC/LaRC
Program/Project/Organization Liaisons		
Mr. Chuck L. Davis	Propellants	KSC
Mr. Regor L. Saulsberry	Propulsion	JSC WSTF
Administrative Support Personnel		
Mr. Eric Pope	Technical Writer	ATK/LaRC

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4.0 Executive Summary

The Johnson Space Center (JSC) White Sands Test Facility (WSTF) and NASA Engineering and Safety Center (NESC) were requested by Mr. William Gerstenmaier (NASA Associate Administrator for Space Operations) to perform an evaluation of a proposed hydrazine/monomethylhydrazine (MMH) fuel treatment method using alpha-ketoglutaric acid (AKGA). This evaluation request was prompted by preliminary tests at the Kennedy Space Center (KSC), suggesting cost and operational benefits to NASA for the Space Shuttle Program (SSP) and other hardware decontamination and decommissioning, in addition to hydrazine and MMH waste treatment activities. WSTF and NESC coordinated their efforts and developed a quick-response team including chemists from within their organizations and from industry (CH2M HILL). The team developed questions related to the operations, processes and chemical reactions to determine what work had been performed, and what information was available by the holder of a patent (New Mexico Highlands University [NMHU]) for the process, and KSC where experimental work is being performed. These questions were forwarded and subsequently discussed with the NMHU patent holders and KSC personnel. This paper provides the team's position on the current KSC and NMHU efforts toward implementing the AKGA treatment technology with flight hardware, ground support equipment (GSE), hydrazine and MMH spills, and vapor control. This evaluation is current to the last data examined (approximately September 2008).

The majority of this work is based on the NMHU patent claims, not all of which have been experimentally demonstrated or validated, and their practicable implementation remains to be proven. AKGA was found to treat hydrazine and MMH solutions under certain conditions in the laboratory, resulting in reduced fuel concentrations in solution, and the vapor phase when scrubbed. Reduction of hydrazine vapor off-gassing from contaminated components, such as Teflon® seals, after AKGA treatment has also been demonstrated in preliminary tests. Tests with MMH are planned. Although reduction in hydrazine and MMH concentrations were observed, AKGA-hydrazine and AKGA/MMH reaction products have not been fully characterized.

Complete characterization of reaction products and waste characterizations is required to satisfy the Florida Department of Environmental Protection (FDEP) requirements for waste profiles. The limited waste characterizations at this time lead to concerns related to proposed reaction product disposal by microbial digestion in wastewater treatment facilities, direct land disposal, or incineration.

The microbial digestion process described in the NMHU patent appears to be based on speculation. The team's literature review found a single 30-year old reference in which one *Pseudomonas* species studied under controlled laboratory conditions degraded the AKGA-hydrazine reaction product. In addition, neither KSC nor NMHU is pursuing the microbial

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digestion process at this time. Complete characterization is also required for acceptance by NASA on the applicability of treating flight hardware and GSE, whether for reuse or decommissioning. Characterization is also required to evaluate corrosion or damage to hardware due to residual acid level, non-volatile residue formation, potential reactivity of AKGA with metals, and general personnel safety if the solutions and their residues are not fully removed from treated hardware.

The AKGA-hydrazine product is relatively insoluble and has been observed to precipitate. Evaluation of precipitate removal or prevention of formation is required to prevent potential blockages in hardware lines, orifices, and screens.

Based on the information gathered by the JSC WSTF/NESC team indicating initial hydrazine and MMH decontamination results (although at relatively low technology readiness levels), there are significant unknowns requiring resolution. The product and waste characterization, microbial treatment process evaluation, hardware effects assessment, and precipitation evaluation must be performed before this project has any chance of succeeding. The relatively low-level of effort given to the project at this time is insufficient to resolve and validate the processes proposed by KSC and NMHU for use with flight hardware and GSE.


The team suggests continued research into the AKGA-hydrazine/MMH neutralization capability, characterization of AKGA-hydrazine/MMH reaction products, and development of processes for decontaminating hardware. Decontaminating flight hardware may be pursued as the process develops and matures, but it is premature to investigate flight hardware without an adequate level of understanding and documentation of the chemical reaction products and the potential deleterious effects on hardware. The opportunity exists for process developers to fully integrate outside stakeholders (FDEP, other NASA Centers, and hardware suppliers) into project reviews to present status, discuss issues, and to ensure project requirements have been identified and are being addressed.

5.0 Task Overview

Note: “Treating”, “treatment”, “remediating”, or “neutralizing” of hydrazine or MMH are nominally synonymous terms for chemical reactions that produce relatively non-toxic, less toxic, less-hazardous or more environmentally benign compounds. The term “neutralization” in this application does not refer to elementary acid/base reactions.

The JSC WSTF/NESC team took the following approach:

- Organize and make assignments within the team based on administrative authority and technical expertise, and establish a schedule for communication and actions.
- Review the treatment processes (the initial reaction of hydrazine with AKGA to produce a pyridazine derivative, catalytic hydrogenation of the pyridazine to produce glutamine, and

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subsequent microbial digestion of glutamine), including experimental conditions and data, as originally proposed in the NMHU patent and described by KSC personnel.

- Review processes, available publications, and data that led to the Space Operations Mission Directorate (SOMD) presentation (Appendix D).
- Develop and discuss questions with NMHU and KSC personnel to understand the hydrazine treatment processes and subsequent product formation.
- Formulate evaluation opinion based on chemical reactions used by NMHU and KSC.
- Provide Findings and Recommendations to the requester with a short turnaround.

The team reviewed the NMHU patent, KSC material (primarily presentations and internal unpublished progress reports [Appendix D]), and relevant literature. A list of questions was next developed with the collective input of the team to elicit the required information from NMHU and KSC to develop this position paper (Appendix A). The questions were ordered into Operations, Processes, Chemical Reactions, and Alternative Processes categories. The list of categorized questions, including a supplemental list on Chemical Reactions, is combined and shown in Attachment A.

The list of categorized questions was submitted to NMHU and KSC personnel in advance of technical interchanges with the team, in order to provide the respective groups sufficient time to develop responses.


The team met with NMHU and then KSC personnel via teleconference to discuss the provided questions and their responses. The team consolidated the responses and discussed them in detail in separate meetings. The responses provided significant insight into the work performed at NMHU and KSC, work in progress, and planned future work. Table 5.4-1 was developed to summarize responses by NMHU and KSC to the list of categorized questions. The responses of each of these organizations, which worked in part independently of each other, are separated accordingly.

5.1 Patent and NMHU Work

Patent

The JSC WSTF/NESC team reviewed the NMHU-held United States (U.S.) Patent 7,074,959 B2 “Methods and Systems for Remediating Hydrazine-Contaminated Equipment and/or Surfaces” (Appendix F) and relevant literature including “A New Synthesis of DL-Glutamine” (G. Bruce Kline and Standiford H. Cox, J. Org. Chem.; 1961; 26(6) pp 1854 – 1856), U.S. Patent 2,873,294 “Process for Synthesizing Glutamine”, and “Bacterial Utilization of a Hydrazine Derivative as Nitrogen Source for Growth” (T.A. LaRue and J.J. Child, Can. J. Microbiol.; 1979; 25(7) pp 822-825).

NMHU patented a process for the remediation of hydrazine-contaminated equipment and/or surfaces. This process is generalized in Figure 5.1-1.

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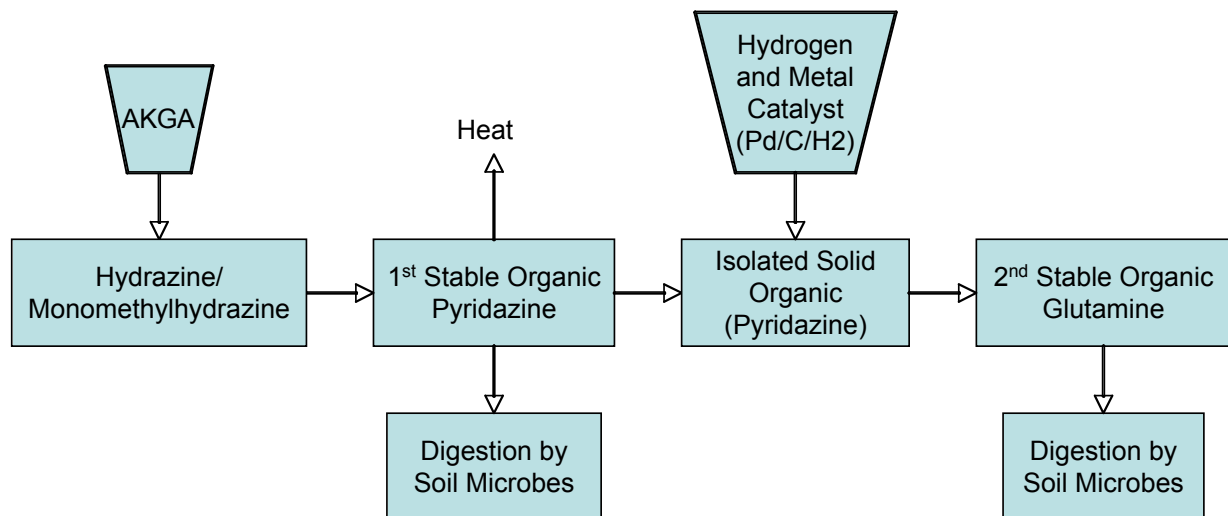
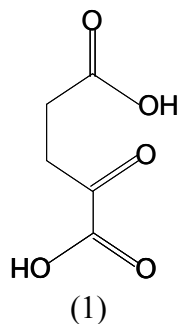



Figure 5.1-1. Proposed Hydrazine Neutralization Process Flow Diagram

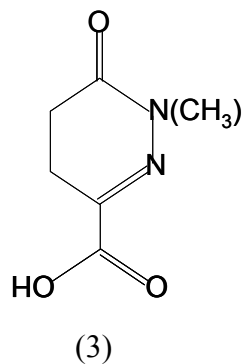
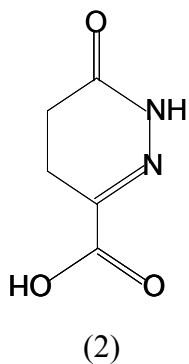
This patent contains numerous and broad claims, many of which have yet to be substantiated by NMHU. The claims are summarized as follows:

AKGA (1) solution is applied to a hydrazine- or MMH-contaminated object or spill. The methods of application are broad, ranging from in-situ application on the ground to direct application to a contaminated object.



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The subsequent reactions between AKGA and hydrazine or MMH produce pyridazine derivatives (2) and (3):



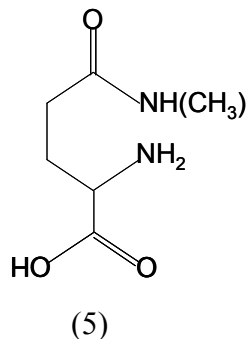
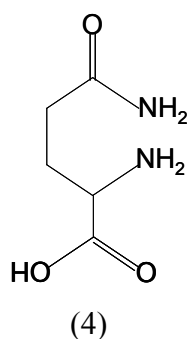
Where:

(2) 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (PCA)


(3) 1-methyl-1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (MPCA)

The NMHU patent claims that PCA and MPCA may be digested by soil microbes, although this appears conceptual only. In addition, the specific microorganism(s), the conditions of digestion, and the products of microbial digestion are not given. No data related to the microbial digestion process was provided in the patent or elsewhere by NMHU.

The pyridazine derivatives are then catalytically hydrogenated by an unspecified metal catalyst and hydrogen (H) to their corresponding glutamines. PCA yields glutamine (4) and MPCA yields glutamic acid 5-methylamide (N-methylglutamine) (5):



U.S. Patent 2,873,294 "Process for Synthesizing Glutamine", which is not referenced in the NMHU patent, describes a process whereby hydrazine and MMH (in addition to other hydrazine derivatives), are reacted with AKGA to yield PCA and MPCA respectively (in addition to other

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substituted pyridazines). The PCA and MPCA are then isolated and catalytically hydrogenated with a palladium (Pd) catalyst (including Pd on carbon (C)), and H to produce glutamine and N-methylglutamine, respectively. This process was patented in 1959. No evidence was found by the JSC WSTF/NESC team that the process was implemented or employed beyond the patent stage.

According to NMHU patent claims, the glutamine and N-methylglutamine may then be digested by soil microbes. The final products of microbial digestion are not identified or discussed, which suggests the microbial digestion claim is only a claim and has not been demonstrated or validated by NMHU.

Process Evaluation

In-situ (at the spill site) treatment of hydrazine or MMH spills is a process that will require careful evaluation and coordination with state or federal authorities. The products formed by the addition of AKGA to hydrazine or MMH spills will require a thorough hazardous waste characterization. Permits may be required for in-situ treatment.


Catalytic hydrogenation of PCA and MPCA to the respective glutamines will require special equipment and safety precautions. The catalytic hydrogenation process described in the NMHU patent uses a Pd catalyst (5 percent Pd on C), and H. Catalytic hydrogenation is, in general, a typical industrial scale process, which requires appropriate safety and handling precautions for the catalyst and for the H. Commercial hydrogenation units are available and their potential use could be explored. The industrial scale use of H in this synthetic organic chemical route to waste treatment scheme will require careful examination.

In addition, the catalytic hydrogenation of PCA and MPCA will produce two stereo isomers of the respective glutamines (D- and L- enantiomers). Enantiomers are a pair of molecules with the same atoms, but some of the atoms are arranged such that the two molecules are different, non-superimposable mirror images of each other.

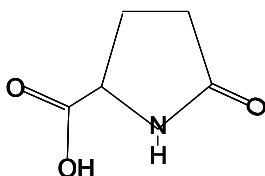
Because metabolic processes are most often stereoselective (one enantiomer is preferred over the other), a microbe, or a combination of microbes, that will degrade both the D- and L- enantiomers will be required.

NMHU Work

NMHU work appears to be best summarized in the NMHU patent. Although responses to the questions were provided verbally, no publications and limited data were made available for team review. NMHU personnel offered a discussion of additional options, including the examination of microbial digestion of pyridazine derivatives without the catalytic hydrogenation step, and the potential commercial aspects of isolating and selling the pyridazine derivatives as commodity products. Another conceptual option presented by NMHU was to obtain pyroglutamic acid (6). Pyroglutamic acid, which is a cyclized product of glutamic acid also existing in D- and L-

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enantiomers, may be obtained by an unspecified reaction of PCA and could be sold as a commodity product (plant growth enhancer). NMHU presented no evidence to substantiate the commercial viability of this option. A market survey would have to be performed to determine the salability of any products.



(6)

The team was unable to ascertain certain elements of the process that are essential to a mature technology. These include:

- All work was limited to laboratory bench scale tests.
- Applicability to field conditions was not performed, including decontamination and cleanup of spills on ground and soil.
- Characterization of PCA and MPCA reaction products is not complete.
 - The NMHU patent states (with respect to the reaction of AKGA and hydrazine: “The reaction generally appears to be a quantitative reaction with the aqueous hydrazine”. There is no discussion of by-products. This statement also suggests the laboratory work with hydrazine including characterization of reaction products was at a preliminary stage.
 - Relatively little work was performed with MMH as compared to tests involving hydrazine.
- Characterization of the catalytic hydrogenation products of PCA and MPCA (and other products of the AKGA/hydrazine and AKGA/MMH reactions that could remain) is not complete.
- NMHU has not evaluated microbial digestion of PCA and MPCA beyond the conceptual stage.
 - The NMHU patent mentions that PCA is not easily biodegraded but the ideal situation would be to find a method for the safe destruction or remediation of PCA, that the use of microbes (e.g. *Pseudomonas* species found in the soil) as a method for the metabolism of a nitrogen-nitrogen (N-N) bond can thus be implemented, but provides no data or reference (e.g. LaRue and Child (1979)) establishing viability of

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- this concept. Implementation is contingent on finding a suitable microorganism, which is not being pursued at this time.
- LaRue and Child (1979) reported the ability of microbes to metabolize the N-N bond seems rare. A *Pseudomonas* species from soil utilized PCA as a C and N source. This appeared to be the first report (as of 1979) and the only one found by the JSC WSTF/NESC team that a microbe can cleave an N-N bond in an organic compound and use the products for growth, and this report is not referenced in the NMHU patent.
 - Marketability aspects of commodity products (PCA, MPCA, and their respective glutamic acid derivatives) appear to be conceptual only.
 - No investigative work on prills or AKGA-coated screens for vapor control has been performed.

Completion of the NMHU work is required to provide the data necessary to adapt these processes to KSC ground operations.


5.2 Kennedy Space Center Work

The scope of the KSC work was narrower than the NMHU work and is focused on specific aspects of KSC ground operations. KSC performed preliminary work with AKGA, hydrazine, and MMH, and is pursuing additional work with the decontamination of hardware and softgoods. Preliminary work was performed using AKGA solutions for vapor scrubbing as a potential alternative to the current citric acid technology in laboratory-simulated tower scrubbers. At the present, a hardware decontamination process is being evaluated for the SSP Orbiter hydrazine Auxiliary Power Unit (APU) and the MMH Orbital Maneuvering/Reaction Control Systems (OMS/RCS) decommissioning.

The potential for reuse of flight hardware will be evaluated in the future due to significant interest in reusable components, as the Constellation Program's Crew Exploration Vehicle (Orion crew module) is planning on using hydrazine for its RCS. For applicability of softgoods decontamination, KSC is in the process of obtaining fuel tanks with AF-E-332 (an ethylene propylene diene modified (EDPM) elastomeric diaphragm and bladder tank material also used in SSP APU systems) from Vandenberg Air Force Base (VAFB), and other components from hardware manufacturer Aerojet, for additional testing.


Information on KSC work was obtained from AKGA briefing charts (Appendix D) and from responses to a categorized list of questions (Appendix A). A summary of the KSC work consists of:

- KSC plans, in general, to examine issues associated with the use of AKGA on flight hardware and GSE. These include compatibility/permeation of AKGA with softgoods, induced/accelerated corrosion of metals, precipitate or deposit formation, non-volatile

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residue (NVR), and whether future flight hardware treated with AKGA solutions could be reused (if intended).

- Decontamination of softgoods is being examined under laboratory conditions. Hydrazine-contaminated specimens (Teflon® and AF-E-332) are immersed in beakers of AKGA solution, removed, and then monitored for airborne hydrazine concentrations over different time periods.
 - Initial experiments have shown some results suggesting the AKGA solution reduced the hydrazine vapor concentrations for varying times (days to weeks). Further testing is in progress to evaluate the limits of detection, reproducibility of results, and to validate the method of detection.
- Additional work is underway for evaluation of hardware decontamination (e.g., convoluted flex hoses and valves).
- Test matrices for decontaminating propellant systems are in development.
- Monitoring of hydrazine vapors above the liquid is being performed using dosimeter badges and Interscans™. A limited number of experiments have been conducted; normalization or standardization of the vapor monitoring methods has not been performed, nor has accuracy or reproducibility of results been verified.
- KSC monitors the extent of hydrazine and MMH degradation in solutions by a gas chromatographic method used to determine hydrazine and MMH remaining in solutions. Other species in the reaction solution may interfere with this determination. No data has been shown validating the gas chromatographic method.
- KSC is not monitoring reaction products due to limitations in test methods. Reaction progress and the effectiveness of hydrazine and MMH decontamination are monitored by measuring the reduction of hydrazine or MMH concentrations in solution or in the reactor headspace. Characterization of the reaction mixture is incomplete. While it is a reasonable assumption that PCA and MPCA are predominant products, the data for product identification (both predominant and minor products) under KSC conditions has either not been completed or formalized. Some raw mass spectral data obtained by NMHU was not clear in its origin (conditions of reactions) or interpretation. Monitoring product concentration in addition to monitoring reactant concentration is required to ensure mass balance is maintained and to ensure complete understanding of product composition.
 - PCA has limited solubility in aqueous solutions and precipitates from the reaction mixture, whereas MPCA remains in solution under KSC-tested conditions.
 - Precipitation will be of concern for the reuse of hydrazine hardware, and may impede the contact of AKGA solution with contaminated surfaces. Tests to determine precipitation of MPCA within interstitial spaces and/or complex propellant tank structures with acquisition screens as found in the SSP OMS/RCS, remain to be performed.

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- Pseudo first order rate constants with respect to MMH and hydrazine have been determined and indicate the neutralization reaction to be relatively rapid (Appendix E).
- Once the reactions are fully characterized and a disposition method has been proposed, the status of the AKGA, hydrazine/PCA, and MMH/MPCA decontamination solutions will be discussed with waste management specialists and the FDEP. The PCA and MPCA profiles are new to KSC, and additional data is required for regulatory characterization.
- The primary goal is to eliminate the existing hydrazine and MMH waste stream. KSC is considering recovering and selling PCA and MPCA, but this is based on NMHU's premises (which are conceptual only).
 - The current KSC waste stream is primarily hydrazine and MMH, but includes small quantities of unsymmetrical dimethylhydrazine (UDMH) from Aerozine-50 (A-50). A-50 is used by the unmanned space program at KSC. KSC currently produces 12,000 gallons of hydrazines (hydrazine, MMH, and UDMH) waste, which also contains isopropyl alcohol (IPA) and diluent water. A-50 is dedicated entirely to the Delta II Expendable Launch Vehicle (ELV) program (second stage propulsion). A-50 residuals are kept separate from MMH and hydrazine residuals until such time they are declared "waste" and fall into the 90-day accumulation cycle. A-50 recovery or recycling is not attempted at KSC and does go into the 90-day cycle.
 - UDMH does not form a pyridazine and treatment of UDMH-containing waste, such as A-50, using AKGA is outside the current scope of KSC work.
- KSC is not investigating catalytic hydrogenation or microbial digestion of pyridazine products. Potential disposal of pyridazine products requires evaluation to verify that effluent from the AKGA treatment of hydrazine and MMH can be treated in a wastewater treatment plant that uses biological treatment processes.
- The KSC focus is not on neutralizing spills.
- AKGA is being considered as a replacement for citric acid for scrubber applications. Precipitate formation of PCA with hydrazine applications will be a performance and maintenance problem in scrubber operations. Minimal effort has been given to scrubber tests, though the concept has been demonstrated with laboratory-simulated tower scrubbers.

The main emphasis of the work at KSC is on hardware decontamination; museum preservation for the SSP Orbiters, and post flight deservicing/decontamination for the new Orion crew module. KSC may look at prills or AKGA-coated screens for propellant vapor control.

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5.3 Additional Discussion

The literature surveys performed were to determine if additional work related to hydrazine neutralization or microbial digestion of PCA/MPCA was available.

Hydrazine and MMH Neutralization

Kline and Cox (1961) reported an 88 percent yield of PCA from the reaction of AKGA with hydrazine hydrate in water, and a 56.5 percent yield of MPCA from the reaction of AKGA with MMH sulfate in water. The AKGA-hydrazine reaction was performed with a slight excess of AKGA; the AKGA-MMH reaction was performed with a twofold excess of MMH. Because the current NMHU and KSC work involves large stoichiometric excesses of AKGA, higher product yields than those obtained by Kline and Cox (1961) are expected. The NMHU patent reported the AKGA/hydrazine reaction generally appears to be a quantitative reaction, but no yield is specified.

Kinetic experiments under pseudo first order conditions (large excess of AKGA) indicate that the reaction may proceed to completion. This determination is limited by detection limits. At this time, the lower detection limit at KSC for hydrazine and MMH in solution is 0.5 mg/L


The KSC reaction mixtures have not been completely characterized, although KSC has provided raw data suggesting PCA and MPCA have been identified as reaction products. The characterization of the reaction products will be required to complete the waste characterization for disposal purposes and to assess the hazards of PCA and MPCA wastes. This characterization may include the determination of residual hydrazine or MMH, salts of hydrazine or MMH, and other products of the reaction with AKGA, hydrazine, and MMH. An industrial hygiene assessment of the toxicity of the products, or the solutions or solids resulting, is necessary. This assessment will likely be required for all health, safety, and environmental perspectives.

In addition, heat generation, and resulting pressure increases, from the reaction of AKGA with hydrazine and MMH must be evaluated.

The AKGA solutions used by KSC have pH values as low as 1.5. This acidity requires safety precautions for handling AKGA solutions in addition to those required for handling hydrazine- and MMH-contaminated hardware and solutions. The pH of the waste solutions must also be known to provide a complete waste characterization in addition to safety precautions for handling treated wastes. There may also be corrosion issues associated with the use of AKGA on hardware not only due to its acidity, but also to its potential to form stable complexes with metal ions including aluminum (Yang et al 2003). Exposure of metals to AKGA solutions could result in inducing or accelerating corrosion.

PCA/MPCA Digestion

LaRue and Child (1979) indicated that PCA was biodegraded in the presence of mannitol, by a *Pseudomonas* bacterial species isolated from garden soil. It is likely that PCA served as a C and

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N source for the bacteria. Glycine formation was indicative of PCA N-N bond cleavage. Bacterial growth was maintained in media containing PCA at a concentration of 5000 mg/L, suggesting that PCA is not deleterious to bacterial growth at this concentration. Biodegradation of MPCA was not tested by LaRue and Child (1979) and there have been no reports of this found in the literature. LaRue and Child (1979) also reported that the ability of microbes to metabolize the N-N bond seems rare, as several other chemicals with N-N bonds were not biodegraded. An extensive literature survey indicated that LaRue and Child (1979) was the only literature cited for PCA. Biodegradation of PCA and MPCA, including methods for determining biodegradation in soil and wastewater, and the determination of biodegradation products will require further characterization to establish this process as a viable option.

5.4 Summary

The JSC WSTF/NESC team took the collective responses of NMHU and KSC personnel to the categorized questions and developed a status table. The table is categorized into the following aspects of the processes described by NMHU and KSC personnel.

1. Hydrazine/MMH Neutralization to PCA/MPCA
2. PCA/MPCA Digestion by Microbes
3. PCA/MPCA Conversion to Glutamines (via Hydrogenation)
4. GSE (Tank Farms, Hardware) Decontamination and Decommissioning
5. Flight Hardware (SSP) Decommissioning
6. Waste Stream/ Rinse Solution (Hydrazine, MMH) Reduction
7. Ground Spill (Soil) Remediation
8. Vapor Scrubbing (Hydrazine, MMH)
9. Vapor Control (Prills, AKGA-coated screens)
10. Personnel Safety Handling and Environmental Compliance

To each of these aspects the status of the work performed to date and the intended work by NMHU (primarily concerning the NMHU patent) and by KSC was briefly summarized. Team comments concerning Risk and Opportunity were provided. A technology readiness level (TRL) was assigned to each aspect of the process in accordance with NASA Policy Requirement (NPR) 7123.1A, "NASA Systems Engineering Processes and Requirements" (Appendix B). A summary of results is shown in Table 5.4-1, NMHU/KSC Summarized Responses.




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Table 5.4-1. NMHU/KSC Summarized Responses


	Aspects	TRL	NMHU (Patent)	KSC	Comments
CHEMISTRY	1 Hydrazine/MMH Neutralization to PCA/MPCA	3	<ul style="list-style-type: none"> -Concept tests performed on a laboratory bench scale provided evidence of neutralization -Limited data on hydrazine and MMH reactions, and reaction products -Determined temperature rise as a function of AKGA concentration 	<ul style="list-style-type: none"> -Concept tests performed on a laboratory bench scale provided evidence of neutralization -Limited data on hydrazine and MMH reactions and reaction products -Reaction progress monitored by disappearance of hydrazine and MMH, characterization data limited 	<p>Risk</p> <p>1 Disposal of PCA and MPCA is contingent on waste characterization and permitting by NASA and FDEP. Additional data may be required. If treated in wastewater treatment plant, need to determine impact on wastewater bacteria.</p> <p>2 Precipitation characterization incomplete due to limited data provided; NMHU has products from both reactions provided by KSC but no data has been reported</p> <p>3 Evaluation of flight hardware before verifying hydrazine (and MMH) decontamination and characterizing reaction products</p> <p>4 Heat generation due to exothermic reactions</p> <p>5 Potential analytical error</p> <p>Opportunity</p> <p>1 Possible sale of PCA and MPCA (will depend on regulatory determinations; additional data likely required).</p> <p>2 Further characterization of MMH reaction and reaction products</p> <p>3 Pending waste characterization, possible opportunity for disposal of AKGA-treated hydrazine and MMH wastes as non-hazardous wastes and at cost savings over existing process</p>

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	Aspects	TRL	NMHU (Patent)	KSC	Comments
CHEMISTRY	2 PCA and MPCA Digestion by Microbes	1	-Appears conceptual only; no testing or data to report. - Patent briefly discusses advantages and possible use of Pseudomonas species	-Outside KSC scope	Risk 1 Technology is conceptual, not demonstrated 2 Technology more complicated than anticipated (cannot simply leave treated spill on the ground; biological reactors required); technology not favored with respect to incineration or other disposal techniques 3 Permits not obtained from NASA or FDEP for treatment or spill control 4 Biological digestion products not identified 5 Only one report on the microbial digestion of PCA found in the literature; no reports of MPCA found Opportunity 1 Develop and prove technology
CHEMISTRY	3 PCA and MPCA Conversion to Glutamines (via Hydrogenation)	3	- Appears to have only been cursorily evaluated by NMHU on a laboratory bench scale -No data to evaluate this process, including identification of end products	-Outside KSC scope	Risk 1 None – outside KSC scope. Any chemistry beyond initial PCA or MPCA formation may not be required for KSC applications (but additional verification of PCA or MPCA reaction products is required). Opportunity 1 Expand scope if required as results may be sale or use of plant growth enhancer purported as another product available from the addition of an oxidation step. This conversion may require more resources and expense, potentially generates more waste.

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	Aspects	TRL	NMHU (Patent)	KSC	Comments
APPLICATION	4 GSE (Tank Farms, Hardware)	2	- Not known if work performed on GSE; may participate with KSC in testing	-Concept work with GSE-type materials (convoluted SS hoses, Teflon®-bore flex hose, coupons) initiated -Working with other Centers to obtain GSE -Methods of AKGA application limited to laboratory bench immersion or filling flex hose with solution -Hydrazine vapor concentration reduced below limits of detection of methods used	Risk 1 Precipitate, if formed, is a problem only for hydrazine application. Precipitation characterization reveals that precipitate is a shortcoming to the process (blocks passages, prevents diffusion of AKGA solutions, complicates drainage) 2 Decontamination not complete; residual hydrazine or MMH permeating from soft goods 3 Corrosion or damage to hardware from AKGA exposure 4 Need to verify completeness of hydrazine (or MMH) decontamination 5 Heat generation due to exothermic reactions 6 AKGA NVR complications Opportunity 1 Complete reaction characterizations 2 Prove process on GSE

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	Aspects	TRL	NMHU (Patent)	KSC	Comments
APPLICATION	5 Flight Hardware (SSP Orbiter) Decommissioning	1-2	- No work performed on flight-like hardware - NMHU may participate with KSC in testing	- Attempting to obtain flight or flight-like hardware from other Centers and VAFB - Mock-up flight-like hardware (contaminated soft goods, flex hoses, coupons, etc) testing in work by KSC - Methods of AKGA application speculative only since flight hardware not tested	Risk 1 Flight hardware not available or allowed at this stage of development 2 Precipitate, if formed, is a problem only for hydrazine application. Precipitation characterization reveals that precipitate is a shortcoming to the process (blocks passages, prevents diffusion of AKGA solutions, complicates drainage) 3 Decontamination not complete; residual hydrazine or MMH permeating from soft goods or trapped in interstitial regions. 4 Corrosion or damage to hardware 5 Need to verify completeness of hydrazine (or MMH) treatment. 6 Heat generation due to exothermic reactions 7 AKGA NVR complications Opportunity 1 Complete testing with mockup hardware 2 Prove process on flight hardware

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	Aspects	TRL	NMHU (Patent)	KSC	Comments
APPLICATION	6 Waste Stream/ Rinse Solution (Hydrazine, MMH) Reduction	3	-May be outside of NMHU scope	-Currently managed as hazardous waste -Discussion with FDEP pending/in work	Risk 1 Waste stream requires further characterization 2 Waste stream requires additional treatment 3 Waste stream requires additional verification/documentation prior to disposal per FDEP (and it is not known whether it can be disposed to sewer or must be containerized and incinerated) 4 Waste stream of limited advantage over existing waste stream, if characterized as hazardous Opportunity 1 Complete characterization of waste stream 2 Possible reduction in volume and hazard 3 Cost savings 4 PCA is commercially available and no supplier has been found for MPCA. Market opportunities may exist.

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	Aspects	TRL	NMHU (Patent)	KSC	Comments
APPLICATION	7 Ground Spill (Soil) Remediation	3	-Appears primarily conceptual -No data shown	-Outside immediate KSC scope -Limited testing performed in laboratory bench scale	Risk 1 Technology not adequate for ground spill 2 Permits not obtained for ground spill remediation. 3 No information on in-situ microbial digestion of PCA or MPCA Opportunity 1 Perform additional testing 2 Present results to FDEP (technology may be successful for ground spill remediation and permitted for ground spill remediation) 3 Pending waste characterization, possible opportunity for in-situ treatment of hydrazine and MMH spills with resultant product considered non-hazardous waste and at cost savings over existing spill treatment processes

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	Aspects	TRL	NMHU (Patent)	KSC	Comments
APPLICATION	8 Vapor Scrubbing (Hydrazine, MMH)	3	-No data shown	-Initial work performed on a laboratory bench scale; additional work required -In some cases precipitate was formed with hydrazine	Risk 1 None other than resource expenditures; existing citric acid scrubbing appears adequate and acceptable within established limitations and procedures 2 PCA precipitation interferes with hydrazine scrubber and scrubbing; no interference was observed from MPCA during MMH scrubbing. The current KSC scrubbing process does not separate the MMH and hydrazine waste streams; presence of hydrazine in MMH waste stream may result in precipitation of PCA. 3 Scrubbing may in part result from formation of acid salts (analogous to citric acid), resulting in hydrazine or MMH salts rather than potentially non-hazardous PCA and MPCA, respectively 4 No apparent advantage if AKGA scrubber waste must be managed as hazardous waste similar to the current citric acid scrubber waste Opportunity 1 Potential improvement over citric acid technology presently in use if waste scrubber liquor can be treated as non-hazardous waste or in a wastewater treatment plant
APPLICATION	9 Vapor Control (Prills, AKGA-Coated Screens)	1	-No data shown	-Possible future work	Risk 1 No immediate risk Opportunity 1 Develop method for prill preparation (e.g., liquid AKGA condensed on the surface of a screen) 2 Develop and validate method for vapor control


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	Aspects	TRL	NMHU (Patent)	KSC	Comments
SAFETY AND ENVIRONMENTAL	10 Personnel Safety Handling and Environmental Compliance	3	-Safety and environmental precautions not necessarily in accordance with NASA requirements	-Safety precautions require review by KSC Safety and Industrial Hygiene -Waste profiles being evaluated by FDEP for waste permit determinations	Risk 1 Personnel exposure (precautions must be taken in accordance with KSC safety requirements) 2 Physical hazards, such as overpressure consequences of heat generation in various configurations (such as entrapment areas in hardware) Opportunity 1 Health and toxicity risk assessments and readiness reviews for field operations performed and approved in accordance with KSC requirements on characterized reactions and reaction mixtures 2 Pending waste characterization, possible opportunity for disposal of AKGA-treated hydrazine and MMH wastes as non-hazardous wastes and at cost savings over existing process


6.0 Findings, Observations, and Recommendations

6.1 Findings

- F-1.** The objectives, priorities, schedules, respective roles and data deliverables of NMHU and KSC, are at early stages and must be clearly defined as this project matures.
- F-2.** AKGA treats hydrazine and MMH under certain conditions, by reducing their concentration, yet their reaction products (neutralized pyridazines: PCA and MPCA) are not fully characterized.
- Realization of waste reduction benefits and safety in handling waste products will depend on sufficient waste characterization to allow FDEP and KSC safety and industrial hygiene to make the further determinations on waste disposal and safety. Additional data on PCA and MPCA products are required. Analytical methods for the determination of AKGA and pyridazine products (PCA and MPCA) need to be developed, validated, and implemented for the characterization of reaction products and wastes generated by the AKGA treatment processes at KSC.

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- F-3.** The AKGA, PCA, and MCPA waste stream has not been fully assessed by FDEP and Environmental Protection Agency (EPA).
- One of the primary points of this work was cost savings by the elimination of a hazardous waste stream. KSC does not approve treatment methods and may require FDEP and EPA input. Additionally, if AKGA were to be applied to the land in efforts to neutralize hydrazine or MMH spills to PCA or MPCA, respectively, there are other regulations that must be considered including the land ban requirements. There may be recycling exemptions that apply due to the material not being a waste or to exemptions in the regulations, but these require FDEP and EPA approval. Similar considerations for MPCA would apply but have not yet been addressed.
- F-4.** Microbial digestion of hydrazine/MMH neutralized pyridazines (PCA and MPCA) has not been demonstrated sufficiently to warrant operability status. No plans for evaluating microbial digestion of PCA and MPCA are evident.
- Conceptual only at this point, evaluation of microbial digestion of PCA and MPCA generated by reactions of AKGA with hydrazine or MMH is essential for development of handling of wastewater and treated spills if this digestion process is considered. Although, NMHU has performed preliminary evaluation, there is no discussion of microbial digestion in KSC task planning.
 - LaRue and Child (1979) reported the ability of microbes to metabolize the N-N bond seems rare. A *Pseudomonas* species from soil utilized PCA as a C and N source. This appeared to be the first report (as of 1979) that a microbe can cleave an N-N bond in an organic compound and use the products for growth. Glycine formation was indicative of PCA N-N bond cleavage. No other reports in the literature were found concerning biodigestion of PCA and none were found for MPCA.
 - A suggested approach for determining biodegradability of PCA and MPCA and evaluation of possible deleterious effects, such as harm to organisms used in wastewater treatment, is presented in Appendix C.
- F-5.** An assessment on the compatibility of AKGA (due to the acidity and chemical nature) has not yet been performed on GSE and flight hardware.
- Testing with components is planned. If adverse effects are observed, hardware cannot be reused. A reuse qualification process would be required.
- F-6.** Decontamination of flight hardware and GSE using the AKGA treatment process requires further development and validation. Considerations apply not only to effective hydrazine and MMH removal, but also to hardware integrity preservation in the case of reusable parts.

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- Soft goods are difficult to decontaminate. Tests with prepared specimens (Teflon and AF-E-332 contaminated with hydrazine) indicate a reduction of vapor phase hydrazine based on testing with dosimeter badges. Specimens exposed to hydrazine or MMH fuels for extended times, as in bladder-containing fuel tanks, must also be evaluated. KSC is in the process of obtaining bladder-containing fuel tanks from VAFB and hardware from Aerojet. Tests with these and with other materials will be required to validate the method. Hardware (metallic components) is less difficult to decontaminate than soft goods, but corrosion and compatibility issues must be addressed. In addition, introducing AKGA solution to the interior of assembled articles, which may require additional decontamination, must be considered. The method of introduction must ensure that all contaminated surfaces are wetted and left in contact with AKGA for a sufficient time for decontamination to occur. A method of verifying decontamination must be used to provide assurance the treatment was satisfactory. Apparent decontamination may be a transient phase, as softgoods containing residual hydrazine or MMH will offgas. Similarly, any areas of entrapment even in hard lines, valves, or other assemblies will be sources of residual hydrazine or MMH. Process reviews with stakeholders and other concerned parties will benefit the approaches to decontaminating flight hardware and GSE.


F-7. Decontamination of flight hardware for museum preservation using the AKGA treatment process requires further KSC development and validation.

- This is the goal of KSC work and has not yet been directly addressed. While residual hydrazine and MMH contamination must be controlled so as not to present a safety hazard to museum personnel and visitors, avoidance of damage to the articles is highly desired to satisfy museum requirements. Museums prefer their specimens to be as intact as possible.

6.2 Observations

O-1. Insoluble reaction products (precipitate formation) are observed from the reaction of AKGA with hydrazine. PCA precipitation occurs with hydrazine but MPCA precipitation has not been observed with MMH over a wide range of concentrations.

- Precipitates in some cases can clog orifices, screens, lines, and interfere with solution hydrodynamics. Consequences of precipitates can be detrimental to flowing solutions and to scrubber performance.
- The apparent lack of MPCA precipitation reduces the probability of clogging screens. This may be important for decontaminating SSP Orbiter OMS/RCS propellant tank screens.

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O-2. Hydrazine vapor control using prill or AKGA-coated screens technology was suggested by KSC, but little work has been done. This is presently not a high priority application at KSC.

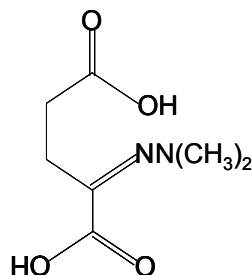
- Methods for propellant vapor control may be useful and additional consideration to this potential application should be considered. Tests must be designed to look at the trapping efficiency of the prills and AKGA-coated screens. Lifetime and mechanical stability of the prills and hazardous waste characterization of spent prills and AKGA-coated screens will also need to be evaluated. Other configurations of vapor control, such as adsorbent pillows, may also be considered.

O-3. AKGA is soluble in water and concentrations up to 4.0 M (584 g/L) have been investigated by KSC.

- Viscosity of concentrated AKGA solutions may have an effect on reaction rate and product formation with hydrazine and MMH. KSC has tested different molar ratios of AKGA with hydrazine and MMH, but has not measured viscosities. Viscosity will be an important factor with the OMS/RCS propellant tank screens and with capillary effects on dead-end tubing, such as flight pressure transducers.
- The higher the AKGA concentration the greater the quantity of NVR.


O-4. Unsymmetrical dimethylhydrazine (1,1-dimethylhydrazine, UDMH) is not within the KSC scope of work.

- UDMH does not form a cyclic pyridazine derivative. A condensation reaction is expected, and is claimed in the patent. This reaction or others that might be predicted (carbohydrazides and acid/base reaction products) should not be discounted for the potential use of AKGA for UDMH decontamination. The AKGA-UDMH product proposed in the patent is (7).



(7)

- Additional work is required to characterize the reaction of AKGA with UDMH, to characterize the efficacy of the decontamination process, and to characterize the

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behavior of the UDMH reaction product in a decontamination process. A hazardous waste characterization is similarly required. An opportunity exists to expand the utility of AKGA to all the hydrazine fuel family. UDMH is a relatively small waste stream dedicated to Delta II rocket second stage (in A-50). Delta II has approximately 3 years of flight remaining. Decommissioning of Delta II systems will be required, but AKGA chemistry is not being examined at this time.


6.3 Recommendations

To raise the TRL levels for process aspects addressed in Table 5.4-1, NMHU/KSC Summarized Responses, the following recommendations are offered.

- R-1.** KSC/NMHU should continue to conduct experiments to fully characterize AKGA-hydrazine/MMH reactions and reaction products. (*F-2, F-3, O-1*)
- R-2.** KSC/NMHU should complete hazardous waste evaluations and determine appropriate options for use (salability) or disposal (microbial digestion) as applicable. (*F-4*)
- R-3.** KSC should take the opportunity to fully integrate process reviews with stakeholders outside of KSC. (*F-5, F-6, F-7*)
 - Input from organizations external to KSC may benefit this effort. Other Centers (such as JSC) and hardware suppliers (such as Boeing) may have similar initiatives, and it would be a benefit to the Agency to have representation from other concerned parties.
- R-4.** KSC should continue to develop standard processes for decontamination of articles and assemblies leading to flight hardware. (*F-6, F-7*)
 - Methods of applying or introducing AKGA solution into a test article are not fully developed. Heat evolution and the viscosity of AKGA solutions must be addressed in development of decontamination processes. The engineering aspects of decontaminating complex hardware as well as the potential consequences to hardware reuse, or resealing for museum preservation, should be considered.
- R-5.** KSC should clearly define or redefine a technical plan to include objectives of this work, prioritize objectives, eliminate aspects that will not be pursued, clearly define the respective roles of NMHU and KSC, and identify and schedule the data deliverables. (*F-1 through 7, O-1 through 4*)

This applies to all aspects of this project including:

- Reaction and reaction product characterization
- Waste characterization


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- Spill remediation
- Vapor control
- Catalytic hydrogenation of PCA and MPCA
- Biological digestion of PCA, MPCA, and glutamines
- Reclamation and sale of potential commodity products (PCA, MPCA, pyroglutamic acid)
- Evaluation of decontamination of hardware and soft goods
- Evaluation of precipitate and NVR considerations
- Evaluation of AKGA corrosion of metals
- Evaluation of reuse of hardware including flight hardware and GSE including the development and implementation of a validation process

This effort should include a detailed test plan, cost estimate, and schedule for executing the tests. This test plan should be reviewed by NASA budget authorities and funded according to the needs of the agency. Otherwise, this project should remain an in-house KSC effort and not be regarded or perceived as the single agency-wide developing solution to SSP Orbiter decontamination and decommissioning efforts.

7.0 Definition of Terms


Corrective Actions	Changes to design processes, work instructions, workmanship practices, training, inspections, tests, procedures, specifications, drawings, tools, equipment, facilities, resources, or material that result in preventing, minimizing, or limiting the potential for recurrence of a problem.
Finding	A conclusion based on facts established by the investigating authority.
Lessons Learned	Knowledge or understanding gained by experience. The experience may be positive, as in a successful test or mission, or negative, as in a mishap or failure. A lesson must be significant in that it has real or assumed impact on operations; valid in that it is factually and technically correct; and applicable in that it identifies a specific design, process, or decision that reduces or limits the potential for failures and mishaps, or reinforces a positive result.

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Observation	A factor, event, or circumstance identified during the assessment that did not contribute to the problem, but if left uncorrected has the potential to cause a mishap, injury, or increase the severity should a mishap occur. Alternatively, an observation could be a positive acknowledgement of a Center/Program/Project/Organization's operational structure, tools, and/or support provided.
Problem	The subject of the independent technical assessment/inspection.
Proximate Cause	The event(s) that occurred, including any condition(s) that existed immediately before the undesired outcome, directly resulted in its occurrence and, if eliminated or modified, would have prevented the undesired outcome.
Recommendation	An action identified by the assessment team to correct a root cause or deficiency identified during the investigation. The recommendations may be used by the responsible Center/Program/Project/Organization in the preparation of a corrective action plan.
Root Cause	One of multiple factors (events, conditions, or organizational factors) that contributed to or created the proximate cause and subsequent undesired outcome and, if eliminated or modified, would have prevented the undesired outcome. Typically, multiple root causes contribute to an undesired outcome.

8.0 Acronyms List


A-50	Aerazine-50 (50% UDMH and 50% hydrazine)
AKGA	Alpha-Ketoglutaric Acid
APU	Auxiliary Power Unit
C	Carbon
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EDPM	Ethylene Propylene Diene Modified
EPA	Environmental Protection Agency
FDEP	Florida Department of Environmental Protection
FTIR	Fourier Transform Infrared Spectroscopy
GSE	Ground Support Equipment
H	Hydrogen
IH	Industrial Hygiene
IPA	Isopropyl Alcohol
JSC	Johnson Space Center

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KSC	Kennedy Space Center
M	Molar Concentration
MMH	Monomethylhydrazine
MPCA	1-methyl-1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid
N	Nitrogen
NASA	National Aeronautics and Space Administration
NESC	NASA Engineering and Safety Center
NMHU	New Mexico Highlands University
N-N	Nitrogen-nitrogen
NPR	NASA Policy Requirement
NVR	Non-Volatile Residue
OECD	Organisation for Economic Co-Operation and Development
OMS	Orbital Maneuvering System
PCA	1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid
Pd	Palladium
RCS	Reaction Control System
SBR	Sequencing Batch Reactor
SOMD	Space Operations Mission Directorate
SOT	Space Operations Transformation
SSP	Space Shuttle Program
TLV	Threshold Limit Value
TRL	Technology Readiness Levels
TWA	Time Weighted Average
UDMH	Unsymmetrical Dimethylhydrazine
VAFB	Vandenberg Air Force Base
WSTF	White Sands Test Facility

9.0 References


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2. G. Bruce Kline and Standiford H. Cox “A New Synthesis of DL-Glutamine”, J. Org. Chem.; 1961; 26(6) pp 1854 – 1856.
3. Gerd Kaupp and Jens Schmeyers, “Solid-State Reactivity of the Hydrazine-Hydroquinone Complex. J. Phys. Org. Chem. 2000; 13: pp 388-394
4. T.A. LaRue and J.J. Child, “Bacterial Utilization of a Hydrazine Derivative as Nitrogen Source for Growth”. Can. J. Microbiol.; 1979; 25(7) pp 822-825
5. U.S. Patent 2873294 “Patent for Synthesizing Glutamine” (1959)

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6. X. Yang, S. Bi, X. Wang, J. Liu, and Z. Bai, "Multimethod Characterization of the Interaction of Aluminum Ion with α -Ketoglutaric Acid in Acidic Aqueous Solutions". Analytical Sciences, Vol. 19 pp 273-279, February (2003)

Volume II. Appendices


- Appendix A. General Categorized Questions Concerning α -Ketoglutaric Acid Treatment of Hydrazines
- Appendix B. Technology Readiness Levels (TRL)
- Appendix C. Microbial Degradation of PCA and MPCA
- Appendix D. AKGA Briefing Charts provided by KSC
- Appendix E. AKGA Reaction Rate Constant (k) Determination provided by KSC
- Appendix F. New Mexico Highlands University Patent "Methods and Systems for Remediating Hydrazine-Contaminated Equipment and/or Surfaces"

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Appendix A. General Categorized Questions Concerning α -Ketoglutaric Acid Treatment of Hydrazines

Operations

1. Is there a preferred method of applying the α -ketoglutaric acid solution to the solutions and to the hardware (addition of liquid by spray, pouring, immersion, etc.)? Each step adds more rinsing and generates more waste; has this been factored into the overall assessment including the cost analysis?
2. Have the hazards of the α -ketoglutaric acid and solutions thereof been considered and what is the assessment of those hazards as they apply to KSC operations?
3. The benefit analysis in the SOT Proposal slide suggests significant cost savings on a reduced scale; has the cost of α -ketoglutaric acid, Pd/C, reactors, and monitoring reactions been considered? Is the microbial treatment factored into the cost analysis?
4. For spill scenarios and use of α -ketoglutaric acid for spill treatment, will volumes and concentrations be predetermined or will the spill be collected in containers, characterized, and then treated? How fast will α -ketoglutaric acid react with hydrazine in a spill scenario, also taking into account the area of spill, volume of spill, mixing, spill thickness, geometry, and temperature)? Will solutions be diluted so that excessive heat is not generated?
5. The flex hose test results presented in the PowerPoint slides indicated < 0.5 ppm hydrazine was detected; is this an airborne concentration? The 8-hr TWA for hydrazine and MMH is 0.01 ppm ($\mu\text{mol/mol}$), so if 0.5 ppm is an airborne concentration it is 50x higher than the TLV. Has this been assessed by IH personnel for KSC ground operational safety? Permeation of softgoods by hydrazine propellants may limit the ability of α -ketoglutaric acid to treat absorbed propellant.
6. The PowerPoint slide presentation indicates that hydrazine was not detected from an o-ring that had been soaked in hydrazine then α -ketoglutaric acid. How was this testing performed? Was a control used in which the o-ring was soaked in water without α -ketoglutaric acid? How was offgassing measured?
7. Was flex hose and o-ring testing performed with MMH?
8. Has the proposed effort been examined by Environmental/EPA experts? Permits may be required for treatment. Also need to look at what concentration of unreacted hydrazine remains to satisfy Environmental Department requirements, and whether the waste codes associated with the hydrazines carry to the products of the reactions and if so what are the consequences.

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9. Have issues associated with the use of α -ketoglutaric acid on flight hardware as well as GSE been examined? These include compatibility/permeation of α -ketoglutaric acid with softgoods, induced/accelerated corrosion of metals, precipitate or deposit formation, and whether flight hardware treated with α -ketoglutaric acid solutions could be reused for flight (if intended).
10. Have the cleaning aspects of the proposal been tested (i.e. have components been treated with α -ketoglutaric acid then precision cleaning to flight specifications (SE-S-0073) been evaluated)?

Processes

11. Have the hazards of the catalytic hydrogenation been considered and what is the assessment of those hazards as they apply to KSC operations? Has a reactor design been considered? Has the feasibility of this for the intended application been examined and tested?
12. Is recovery and recycling of the Pd/C catalyst been considered?
13. Taking into account reaction efficiencies (percent hydrazines reacted), and anticipated hydrazines concentrations, have volume or mass ratios of α -ketoglutaric acid solutions been determined for KSC operations? Will rinses require analysis prior to the addition of α -ketoglutaric acid to obtain optimum reaction? Additionally, will solutions be analyzed for the corresponding pyridazine prior to catalytic hydrogenation?
14. How will the progress/efficiency of the catalytic hydrogenation be monitored?
15. Have the microbial reactions and the reaction products been characterized, and a reactor identified? Has a mass balance been determined to characterize the extent of microbial degradation to products, and are there any hazardous waste issues associated with the products? A reactor may require temperature and nutrient control; life cycle controls, sterilization, and other considerations. Has the feasibility of this for the intended application been examined and tested?

Chemical Reactions

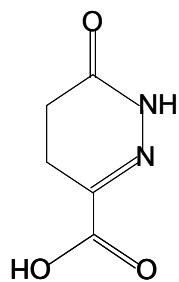
16. What work has been done and published in the literature in the areas encompassing the reactions of α -ketoglutaric acid with hydrazine and MMH, hydrogenation of the product pyridazines to glutamines (derived from hydrazine and from MMH), and microbial degradation of the respective glutamines. Additionally, does the catalytic hydrogenation favor the D- or L- isomer of glutamine, or if both isomers are produced, is the microbial degradation of each isomer equally effective.

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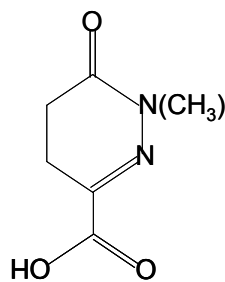
17. Have microbial reactions been proposed for the pyridazines generated from hydrazine or MMH? If not, what microbial process evaluations are planned?
18. What yields of the respective hydrazine and MMH pyridazines and glutamines are produced, and have any other by-products been identified? Were reaction products compared with authentic samples of the expected pyridazines or glutamines?

(Follow up) The structures and chemistry of α -ketoglutaric acid, hydrazine, and MMH suggest more than the corresponding cyclic pyridazine reaction products (1) and (2) are possible. Examples include non-cyclic hydrazones (3) and (4), carbohydrazides (5) and (6) and acid salts, hydrazinium and methyldiazinium α -ketoglutarate, (7) and (8). Formation of acid salts is analogous to the reactions of hydrazine and MMH with citric acid.


Questions include: 1) Have hydrazine- α -ketoglutaric acid and MMH- α -ketoglutaric acid reaction products been characterized? 2) Are FTIR spectra and other characterization data available for review? 2) Have product yields been determined? 3) Have reaction products been compared with authentic samples of the pyridazines? 4) Has variability in reaction products with fuel concentrations been observed? 5) Have studies been performed and/or are there supporting data characterizing the stability of the reaction products over time, and under what conditions? 6) Have studies on the pH dependence of the reactions been performed? 7) Have studies with varying concentrations of α -ketoglutaric acid been performed to evaluate viscosity effects on reaction rate and product formation with hydrazine and with MMH?

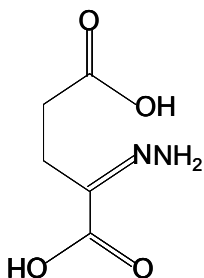


(1)

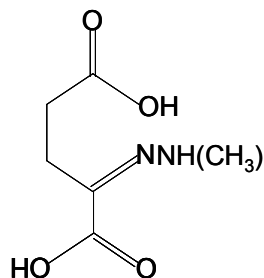


(2)

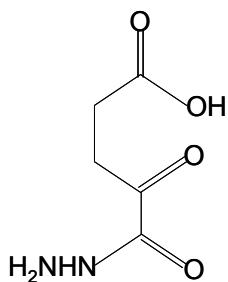
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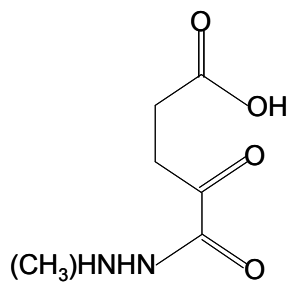
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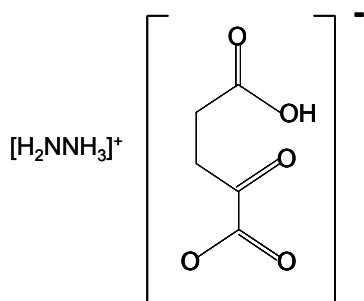
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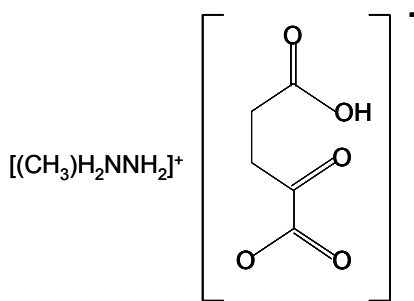
(5)



(6)




(7)



(8)


19. No precipitate formed with hydrazine and MMH vapors at a α -ketoglutaric acid concentration of 0.23M. Is it possible that neither propellant reacted with α -ketoglutaric acid under the conditions tested?
20. Is α -ketoglutaric acid capable of causing a fire with hydrazine or MMH if application is not controlled appropriately? Has heat generation as a function of AKGA and propellant concentrations been investigated?

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21. A precipitate was formed during scrubber simulation testing with hydrazine vapors, but not with MMH vapors at a α -ketoglutaric acid concentration of 0.73M. Is it possible that MMH did not react with α -ketoglutaric acid under the conditions tested?
22. Have the reactions of α -ketoglutaric acid with depleted citric acid scrubber liquors been investigated?

Alternative Processes

23. Have other dicarbonyl or derivatizing agents been considered? What is the advantage of α -ketoglutaric acid over other derivatizing agents?
24. Has catalytic hydrogenation of aqueous hydrazine rinsates been considered (without the use of α -ketoglutaric acid? Predicted products are ammonia for hydrazine and ammonia and methylamine for MMH. This could avoid the use of α -ketoglutaric acid entirely.


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Appendix B. Technology Readiness Levels (TRL)

NPR 7123.1A Appenxix G: Table G-19 – Technology Readiness Levels

	Technology Readiness Level	Description
1	Basic principles observed and reported.	Lowest level of technology readiness. Scientific research begins to be translated into applied research and development. Examples might include paper studies of a technology's basic properties.
2	Technology concept and/or application formulated.	Invention begins. Once basic principles are observed, practical applications can be invented. The application is speculative, and there is no proof or detailed analysis to support the assumption. Examples are still limited to paper studies.
3	Analytical and experimental critical function and/or characteristic proof of concept.	At this step in the maturation process, active research and development (R&D) is initiated. This must include both analytical studies to set the technology into an appropriate context and laboratory-based studies to physically validate that the analytical predictions are correct. These studies and experiments should constitute "proof-of-concept" validation of the applications/concepts formulated at TRL 2.
4	Component and/or breadboard validation in laboratory environment.	Following successful "proof-of-concept" work, basic technological elements must be integrated to establish that the pieces will work together to achieve concept-enabling levels of performance for a component and/or breadboard. This validation must be devised to support the concept that was formulated earlier and should also be consistent with the requirements of potential system applications. The validation is relatively "low-fidelity" compared to the eventual system: it could be composed of ad hoc discrete components in a laboratory.
5	Component and/or breadboard validation in relevant environment.	At this level, the fidelity of the component and/or breadboard being tested has to increase significantly. The basic technological elements must be integrated with reasonably realistic supporting elements so that the total applications (component-level, subsystem-level, or system-level) can be tested in a "simulated" or somewhat realistic environment.
6	System/subsystem model or prototype demonstration in an operation environment.	A major step in the level of fidelity of the technology demonstration follows the completion of TRL 5. At TRL 6, a representative model or prototype system or system, which would go well beyond ad hoc, "patch-cord," or discrete component level breadboarding, would be tested in a relevant environment. At this level, if the only relevant environment is the environment of space, then the model or prototype must be demonstrated in space.
7	System prototype demonstration in an operational environment.	Prototype near or at planned operational system. TRL 7 is a significant step beyond TRL 6, requiring an actual system prototype demonstration in a space environment. The prototype should be near or at the scale of the planned operational system, and the demonstration must take place in space. Examples include testing the prototype in a test bed.
8	Actual system competed and "flight qualified" through test and demonstration.	Technology has been proven to work in its final form and under expected conditions. In almost all cases, this level is the end of true system development for most technology elements. This might include integration of new technology into an existing system.
9	Actual system flight proven through successful mission operations	Actual application of the technology in its final form and under mission conditions, such as those encountered in operational test and evaluation. In almost all cases, this is the end of the last "bug fixing" aspects of true system development. This TRL does not include planned product improvement of ongoing or reusable systems.

Source: Mankins (1995), "Technology Readiness Levels: A White Paper."

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Appendix C. Microbial Degradation of PCA and MPCA

Review of
Microbial Degradation of 1,4,5,6-Tetrahydro-6-oxo-3-pyridazinecarboxylic Acid
and 1-Methyl-1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic Acid


C. P. Leslie Grady Jr. /CH2M HILL

Recommendations for Further Study

The easiest way to determine whether PCA or MPCA has a deleterious effect on biological wastewater treatment systems would be through respirometry. Unacclimated activated sludge from either a full-scale or lab-scale system could be placed in a batch reactor and given a readily biodegradable substrate. By periodically measuring the drop in dissolved oxygen (DO) concentration over time it is possible to establish the oxygen uptake rate (OUR). Once the background OUR has been established, PCA or MPCA could be added and the OUR established again. A drop in OUR upon adding PCA or MPCA would be evidence that they were inhibiting microbial activity. Repeating such an assay at a number of PCA or MPCA concentrations would establish a dose/response relationship. A similar test could be performed with nitrifying activated sludge and substituting ammonia for the readily biodegradable substrate to establish if the compounds are impacted nitrifying bacteria. Volskay and Grady (1988) and Volskay et al. (1990) provide details for such a procedure.

The most rigorous way to establish the biodegradability of PCA or MPCA would be by running an OECD ready-biodegradability test. Electrolytic respirometry is typically used. Respirometric flasks receive mineral salts media containing the compound of interest as sole carbon source at a concentration of 100 mg/L as chemical oxygen demand (COD). The flasks are then seeded with unacclimated seed, either from activated sludge, soil, or some other source. Blank flasks receiving no compound are also set up. Oxygen uptake is followed over time for 20 days and the resulting curve is compared to the curves from the blanks to determine the extent of biodegradation. Because a totally unacclimated seed is used, any organic compound showing biodegradation is considered to be readily biodegradable. Grady (1985) has described this technique. A general overview of biodegradation testing is given in Part I of "Introduction to the Organisation for Economic Co-Operation and Development (OECD) Guidelines for Testing of Chemicals" (<http://www.oecd.org/dataoecd/38/2/5598432.pdf>).

Should a compound not give a positive result in the ready-biodegradability test or if more information is desired about the extent and rate of its biodegradation in a particular environment, simulation tests or inherent biodegradability tests can be used to establish its biodegradability. Both provide for prolonged exposure of biomass to the compound at low concentration. These are frequently done in lab-scale sequencing batch reactor (SBR) activated sludge systems. Typically such systems are started with activated sludge from a municipal wastewater treatment

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plant and acclimated over time to a synthetic wastewater containing the compounds of interest along with other biodegradable organic compounds. Analysis of the effluent for the compound will establish whether primary biodegradation is occurring. If it is, then the biomass can be used in batch tests to establish whether mineralization is occurring as well as information about the kinetics of biodegradation. These batch tests can be done with the compound as the sole carbon and energy source or as one component in a multicomponent mixture. They can be based on removal of the compound (specific analysis) or of COD, or they can be based on respirometry, depending upon the type of information desired. Simulation tests can also be performed with actual wastewaters containing the compound(s) of interest.


Because of the information in LaRue and Child (1979) there is little reason to perform a ready-biodegradability test. Rather, it would be acceptable to move directly to a simulation test using a lab-scale SBR activated sludge system. Concurrent batch tests could be used to establish kinetic data should the need exist.

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Grady, C.P.L. Jr., "Biodegradation: Its Measurement and Microbiological Basis", *Biotechnology and Bioengineering*, **27**, 660-674 (1985).

Volskay, V.T. Jr. and Grady, C.P.L. Jr., "Toxicity of Selected RCRA Compounds to Activated Sludge Microorganisms", *Journal of the Water Pollution Control Federation*, **60**, 1850-1856 (1988).

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Appendix D. AKGA Briefing Charts provided by KSC





Space Operations Transformation

Alternative Hydrazine Fuel Neutralization Technology

Chuck Davis, Hypergol Engineer
KSC-Center Operation Directorate, TA-E3

Edgardo Santiago, Chemical Engineer
KSC-Applied Technology Directorate, KT-D

John Herrington, Engineer/Analyst
NASA TEERM PC, KT-A2



Date:





Space Operations Transformation

Alternative Hydrazine Fuel Neutralization Technology



☐ Background/description:

- § Hydrazine-family fuel residues (whether from decontamination process, spills, or scrubbers) are expensive to treat and dispose by incineration as a highly regulated Hazardous Waste
- § Shuttle ops generate approx. 12,000 gallons of hydrazine haz-waste per year at a annual cost of \$80k. CEV could be expected to generate similar amounts of haz-waste
- § Recently, New Mexico Highland University (NMHU) discovered two chemicals which convert hydrazine into non-toxic byproducts & water § US Pat. 7,074,959 (2006)
- § The objective of this proposal is to demonstrate the applicability of NMHU's discovery to KSC hypergol operations.

☐ Do you know anybody doing similar work or relating to your ideas/proposals


- § None known

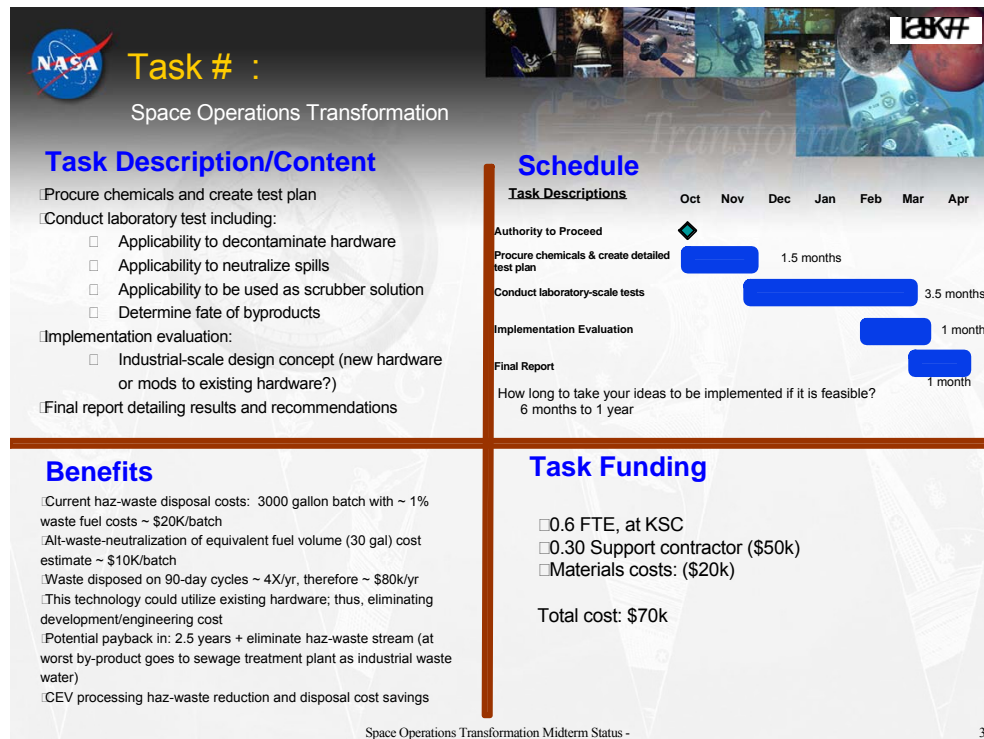
☐ Stakeholders:


- § Stephen Williamson, Wiltech Corp MailCode : WT, (321) 861-2454
 - ☐ Monthly meeting with stakeholders
 - ☐ This technology could be very useful for decommissioning Shuttle systems (starting with Pad B in 2009) and eliminate a major waste stream
 - ☐ Would like to demonstrate viability with small scale testing
 - ☐ Would provide resources to perform field test
- § Tom Draus, NASA MailCode NE-F5, (321) 867-3955
 - ☐ This technology could increase efficiency of hypergol scrubbers and would eliminate the hazardous waste stream.

Space Operations Transformation Midterm Status -

2

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SOMD Transformation Bi-Weekly Status – 11/29/07
Task 3 : Alternative Hydrazine Fuel Neutralization Technology

Accomplishments/Highlights

- ☐ Contractor task orders are completed for both Wiltech and ASRC
- ☐ Wiltech conducted three initial test runs with hydrazine in 2KGA with positive results
- ☐ Revised Wiltech test plan based on initial test results



Issues/Concerns

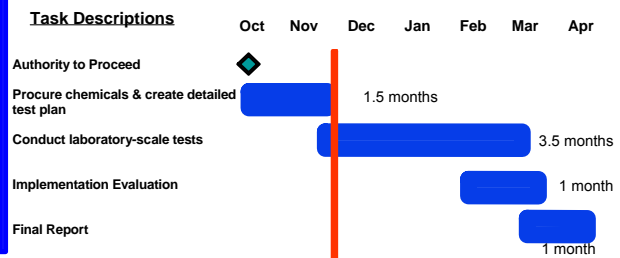
Changes in contractor personnel may impact schedule


Planning for Next Two Weeks

- ☐ ASRC will commence hydrazine vapor neutralization testing ~ Dec 4
- ☐ Wiltech will resume testing after STS-122 launch, ~ Dec 10

Cost/Schedule Performance (Actual Versus Planning)

On schedule



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SOMD Transformation Bi-Weekly Status- 02/21/08
Task 3 :Alternative Hydrazine Fuel Neutralization
Technology

Accomplishments/Highlights

- ☐ Waiting for parts ordered for the scrubber
- ☐ Completed initial high-concentration (Hz) neutralization using ethylacetoacetate (EAA)
 - Neat EAA + Hz → 72 C temperature rise @ ~ stoichiometric mixture ratio = too
 - Diluted w/ ethanol + → manageable 8.6 temp rise @ ~ half stoichiometric mixture ratio
 - Some Hz off
 - Makes cloudy slurry which separated into crystals and EAA-like solution

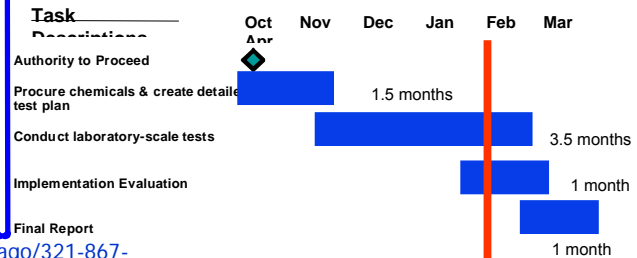
Issues/Concerns

Upcoming Shuttle launch schedule may impact decontamination work


Planning for Next Two Weeks

- ☐ Continue working on building the 1st scale scrubber
- ☐ Characterize Hz/EAA reaction
- ☐ Test diluted Hz (2%) in EAA. This would be more representative of a field-flushed component (e.g. hose, valve or part)

Cost/Schedule Performance (Actual Versus Planned)



Edgardo Santiago/321-867-
 Chuck Davis/321-867-

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SOMD Transformation Bi-Weekly Status – 04/17/08
Task 3 : Alternative Hydrazine Fuel Neutralization Technology

Accomplishments/Highlights

Scrubber tests of AKGA and EAA have shown efficiency similar to citric acid (no detectable hydrazine in the scrubber effluent. However, precipitate has formed with AKGA and EAA. Began tests to identify saturation concentrations at which reaction product precipitates. Started precipitate analysis to identify its chemical formula and confirm the expected chemical reaction. Abandoned sparging tests to measure off-gassing with both EAA, AKGA, & Citric Acid baseline (no neutralization attempted); method ineffective at trapping Hz in citric acid as measured on GC. Successfully neutralized Hz in convoluted SS hose segment w/ < 0.5 ppm residual Hz in solution

Issues/Concerns

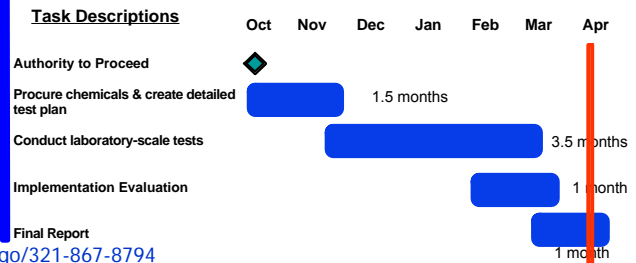
EAA causes the Interscan toxic vapor monitor to read a false positive detection as if it was detecting Hz. The Interscan is used throughout the cleaning process to determine if a part is not that is, has residual Hz on it. Resolving this issue is a whole separate research project. Therefore, Wiltech will focus their efforts exclusively on AKGA testing with Hz for the remainder of this project. AKGA testing has been very positive to date.

Planning for Next Two Weeks


- ☐ Continue working to determine precipitate saturation point in the scrubber system
- ☐ Continue AKGA testing for decontamination of parts, hoses, O-rings, etc.
- ☐ Receive precipitate chemical characterization results from FIT and NMHU

Cost/Schedule Performance (Actual Versus Planning)

Experimental work has extended from the planned time due to delays in building the scrubber.



Edgardo Santiago/321-867-8794
 Chuck Davis/321-867-4748

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Alternative Hydrazine Fuel Neutralization Technology

Space Operation Mission Directorate
Transformation Tasks

Chuck Davis

Center Operations Directorate (TA)

Edgardo Santiago-Maldonado


Applied Technology Directorate (KT)

Presented on May 29, 2008



Background/Description

- ☐ Hydrazine-base waste products are toxic and EPA listed Hazardous Wastes
- ☐ Create ~ 12,000 gallons costing ~ \$112K for disposal per year
- ☐ Shuttle Program decommissioning activities could generate far more waste
- ☐ New Mexico Highlands University issued US Pat. 7,074,959 (2006) for a discovery converting hydrazine into non-toxic byproducts & water
- ☐ **Objective → test NMHU's discovery to KSC hyper-fuel operations**
 - § Estimate ~ \$40K/yr material + ~\$13K/yr labor = \$53K/yr
- ☐ **Non-cost Considerations**
 - § *Eliminate hazardous-waste stream and hazardous operations*
 - § *Preserve Shuttle Orbiters for museum conservation*

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Hydrazine Neutralization Chemistry

Alpha-KetoGlutaric Acid (AKGA) Reaction Characteristics

- Reaction forms neutral product (can precipitate) + water → no gases
- AKGA captures fuel very fast (< 2 minutes)
- Reaction nearly complete < 10 min and complete < 24 hr (<0.5 ppm)
- Can measure with existing sensors (i.e. Interscan, dosimeter, GC)
- Fuel molecules trapped then neutralized → no off-gassing vapors → less risk to personnel

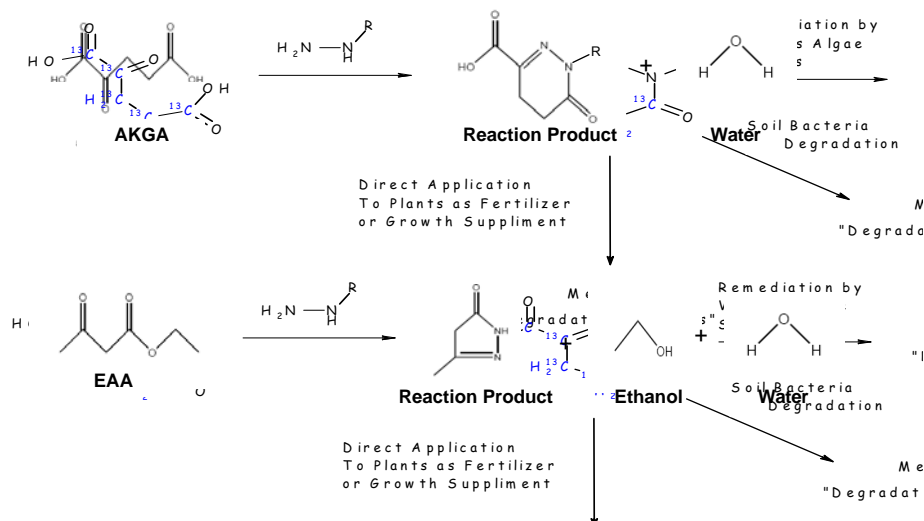
EthylAcetoAcetate (EAA) Reaction Characteristics


- Reaction forms neutral product (precipitate) + ethanol + water
- However, EAA has processing problems
- EAA is a flammable liquid also requiring ethanol to dilute with water
 - Reaction does off-gas Hz and is slow to complete: > 24 hrs to < 0.5 ppm
 - EAA interferes with standard toxic vapor monitor device (Interscan)
 - Reaction product is a gummy precipitate which sticks to hardware complicating future cleaning processes

Therefore, **EAA Implementation not recommended**



Reactions



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Tests & Results Processing Simulation


- Both neutralizers produce solid precipitate
- Conducted worst-case processing scenario
 - § Contaminated 1/2" convoluted SS hose
- **EAA:** After 24 hr, Hz still present
- **AKGA:** Hz not detected (<0.5 ppm)
 - § Precipitate flushed from hose with water
 - § Precipitate dissolves in several commonly used cleaning solvents
- Teflon o-rings soaked Hz for 48 hours then in AKGA for 24 hours → Hz was not detected



Tests & Results Scrubber Simulation

- 1/10th scale scrubber tower
 - § 3" diameter x 29" length
- ~10,000 ppm hypergol vapors generated
- Hypergol quantified at both inlet and outlet
- At 0.73M AKGA & EAA
 - § Solid formed in tower with HZ but not MMH
 - § AKGA solid is soluble in methanol; EAA solid insoluble in most organic solvents
 - § EAA testing discontinued due to solid formation and flammability concerns (EAA+Ethanol)
- At 0.2M AKGA
 - § No precipitate formed with either Hz or MMH
 - § Similar adsorption efficiency as at higher molar ratio



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Summary

- ☐ AKGA is a viable alternative neutralizer for Hz and MMH
- ☐ EAA creates gummy precipitate Š abandoned testing
- ☐ Still waiting on byproduct-fate determination
 - Š Precipitate could have a marketable use as a plant fertilizer
- ☐ *Recommend further testing with AKGA*
- ☐ *Quick Response by KSC Team (Wiltech/ASRC)*
 - Š *Approx. \$63K*
 - Š *(3-4 months)*



Possible Future Work

- ☐ Solid AKGA as a vapor desiccant
 - Š Melting point and liquid viscosity measurements
 - Š Prilling → desiccant tube
 - Š Screen clad w/ AKGA
- ☐ Spill neutralization/clean-up kit
- ☐ Flight-like system decontamination
 - Š Shuttle museum conservation
 - Š AF-E-332 rubber decontamination
- ☐ Attempt to reverse the reaction
- ☐ Develop routine analysis method

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Appendix E. AKGA Reaction Rate Constant (*k*) Determination provided by KSC

Consider the following reaction:

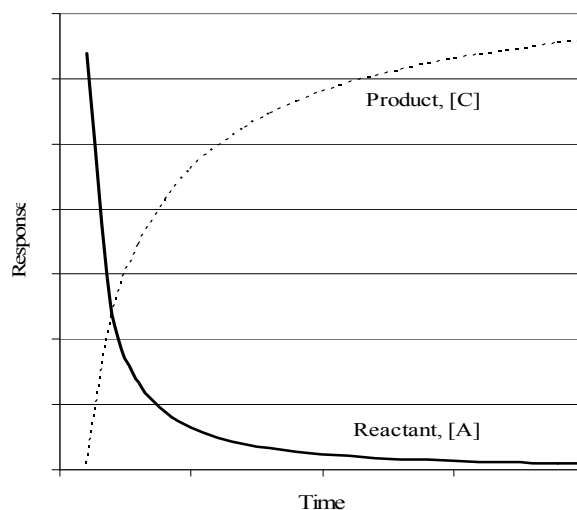


Figure 1


This reaction is graphically represented in Figure 1. An equation relates concentration and reaction rate for any given reaction to a specific, experimentally determined rate constant, *k*. The general rate equation for the aforementioned reaction (1) follows:

$$rate = \frac{d[C]}{dt} = -\frac{d[A]}{dt} = k[A]^m[B]^n \quad (2)$$

where [A] and [B] are reactant concentrations, *m* and *n* represent the order of the reaction with respect to the reactant, and *k* is a rate constant specific to that reaction. Under the conditions [B] >>> [A], the reaction can be simplified as follows:



This is because reactant B is present in such an excess that the change in the concentration of B as the reaction proceeds is negligible compared to that of the change in reactant A. Now, the rate equation can be approached as follows:

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$$rate = \frac{d[C]}{dt} = -\frac{d(A)}{dt} = k[A]^m \quad (4)$$

Which integrates to:


$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^m} = \int_{t=0}^{t=t} k dt \quad (5)$$

At $t = 0$ the concentration of A is $[A]_0$. Thus, the integrated rate equation is:

$$[A] = [A]_0 e^{-k t} \quad (6)$$

It follows that the reaction rate constant k , can be determined experimentally from a plot of $\ln [A]$ versus time.

In this case, reactant “A” is monomethylhydrazine (MMH) and alpha ketoglutaric acid (AKGA) is reactant “B” present in excess. A 100 mL aliquot of 0.25M (11,500 ppm) AKGA was added to a beaker containing a stirring bar and 100 mL of 4.0M (584,000 ppm) MMH. The MMH concentration was sampled and measured by gas chromatography over the course of the reaction. This data is presented in Figures 2 and 3.

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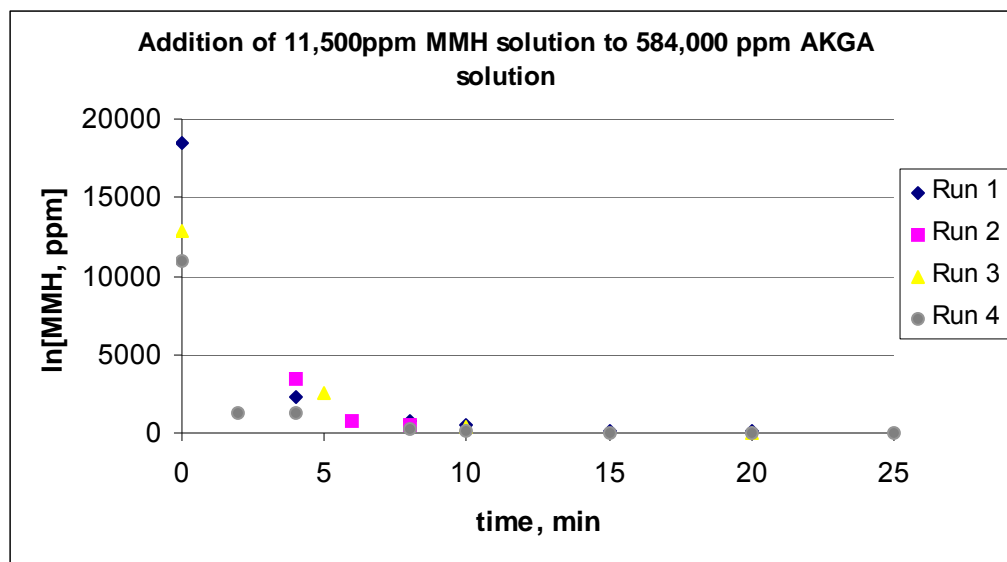


Figure 2

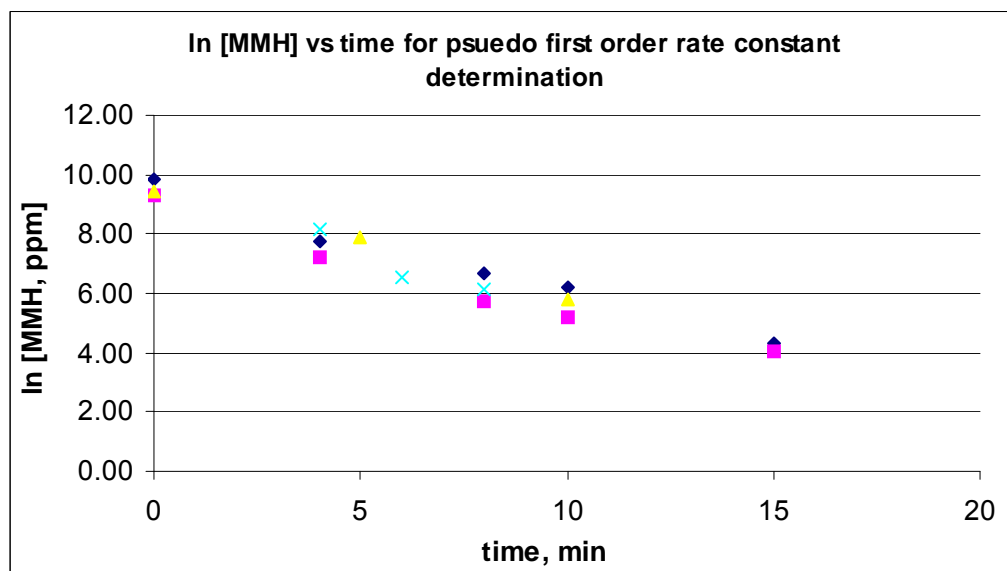




Figure 3

The experimentally determined reaction rate constant k with respect to MMH concentration for the neutralization reaction was found to be 0.3553 min^{-1} . Ongoing work will include confirmation of this value and the rate constant k , for the AKGA neutralization reaction with hydrazine.

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Appendix F. New Mexico Highlands University Patent “Methods and Systems for Remediating Hydrazine-Contaminated Equipment and/or Surfaces”

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US007074959B2

(12) **United States Patent**
Helvenston et al.

(10) **Patent No.:** **US 7,074,959 B2**
(45) **Date of Patent:** **Jul. 11, 2006**

(54) **METHODS AND SYSTEMS FOR
REMEDATING
HYDRAZINE-CONTAMINATED EQUIPMENT
AND/OR SURFACES**

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(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/211,891**

(22) Filed: **Aug. 1, 2002**

(65) **Prior Publication Data**
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(51) **Int. Cl.**
C07C 243/14 (2006.01)

(52) **U.S. Cl.** **564/250**; 540/239; 540/492;
544/239; 588/244; 588/246; 562/563

(58) **Field of Classification Search** 544/239;
540/492, 239; 564/250; 588/244, 246; 562/563
See application file for complete search history.

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Primary Examiner—Shailendra Kumar

(74) Attorney, Agent, or Firm—Luis M. Ortiz; Kermit D.
Lopez; Ortiz & Lopez, PLLC

(57) **ABSTRACT**

Methods of and systems for remediating hydrazine spills,
solutions and hydrazine-contaminated objects including
areas thereof. Initially, an aqueous solution comprising a
dicarbonyl-compound can be prepared. The aqueous solu-
tion can then be provided for application to an object
contaminated with a hydrazine group compound. The hydra-
zine group compounds are converted to a stable organic
compound as a result of a reaction of the dicarbonyl-
compound and hydrazine group compound. Conversion
assists in the remediation of the hydrazine group compound
from the object. The stable organic compound produced as
a result of the reaction between the dicarbonyl-compound
and hydrazine group compound can then be treated with a
metal catalyst and hydrogen to produce glutamine or a
derivative thereof. Both the stable organic compound and
glutamine can undergo microbiological degradation without
further remedial intervention.

20 Claims, 4 Drawing Sheets

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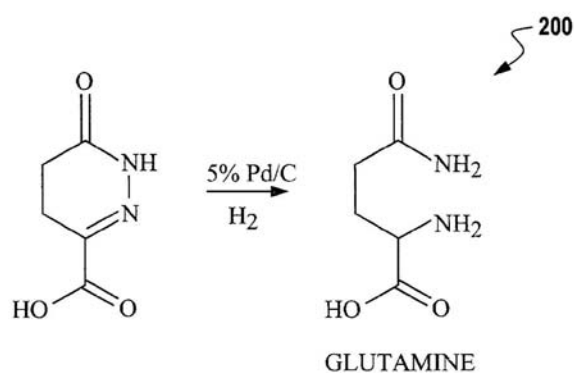
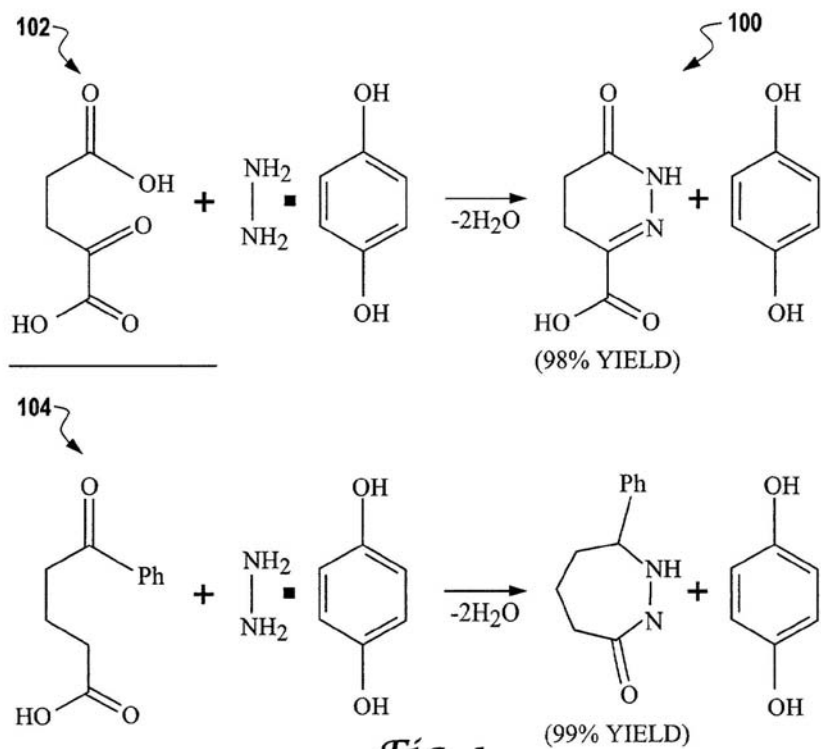



Fig. 2

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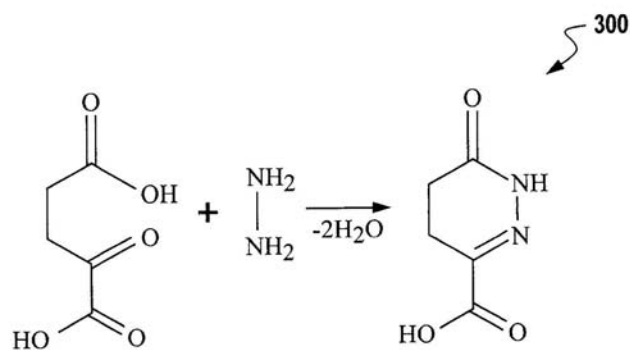


Fig. 3

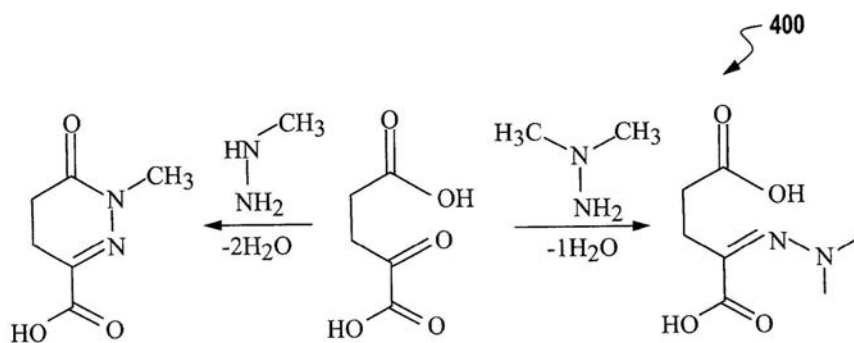



Fig. 4

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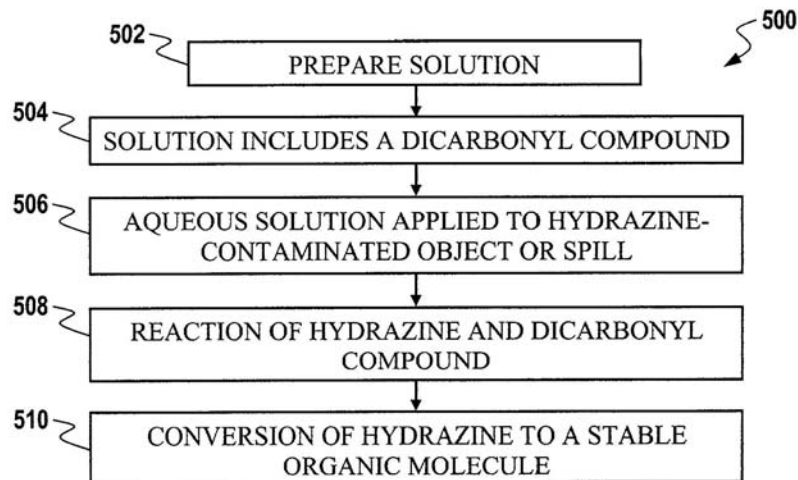


Fig. 5

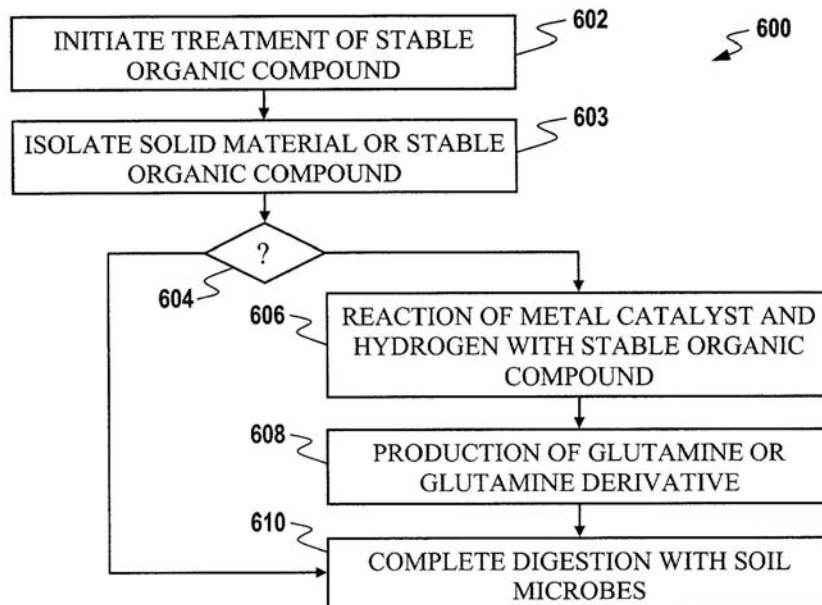


Fig. 6



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700

702

% 2KG	Temperature Rise in C
13.4	19.5
18.19	29.5
22.0	37.5
24.56	39.0
28.3	45.5
34.1	56.0
41.53	62.5
7.62	10.0
0	0

704

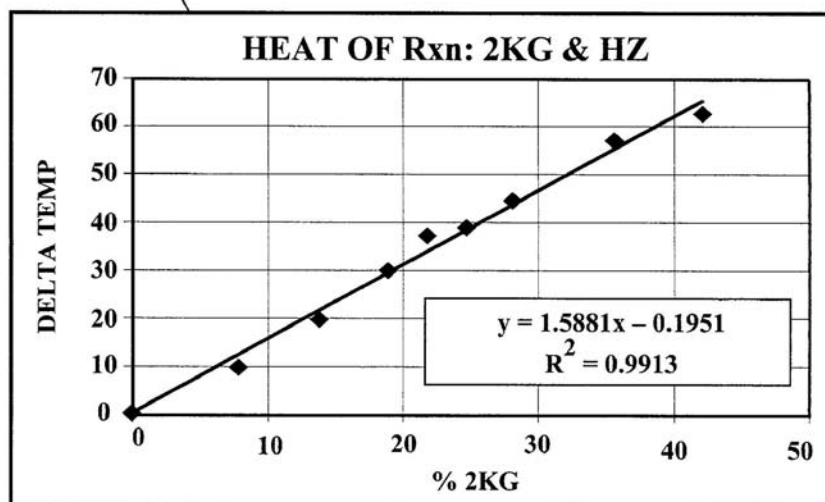



Fig. 7

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METHODS AND SYSTEMS FOR REMEDATING HYDRAZINE-CONTAMINATED EQUIPMENT AND/OR SURFACES

TECHNICAL FIELD

The present invention is generally related to decontamination and remediation methods and systems. The present invention is also related to hydrazine (Hz) and hydrazine-based compounds, such as monomethylhydrazine (MMH) or 1,1-dimethylhydrazine (UDMH). The present invention additionally relates to methods and systems for remediating hydrazine from hydrazine-contaminated objects, including hydrazine contaminated areas thereof. The present invention is also related to dicarbonyl compounds, including dialdehydes, diketones, aldehyde-ketones, aldehyde-acids, aldehyde-esters, keto-acids and keto-esters. The present invention is specifically related to the involvement of the following compounds in remediation of hydrazine: 2-keto-glutaric acid (2KG), 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid (PCA), and glutamine.

BACKGROUND OF THE INVENTION

An environmentally conscious remediation process for the emergency treatment/disposal of hydrazine fuels spills is needed. The highly toxic hydrazine family of fuels is utilized as rocket propellants in virtually all U.S. space programs including both launch vehicles and satellite propulsion systems. Since large volumes of these fuels are annually shipped all over the United States, accidental major spills of these propellants could potentially occur near populated communities during transport over the nation's highways. In addition, smaller spills could also occur during launch operations and storage at the user facilities.

An inadvertent release of hydrazine to the environment can be extremely hazardous due to the mutagenic nature of such chemical compounds, which can induce tumor growth in human beings years following even a low level exposure. Hydrazine compounds are classified as suspected human carcinogens and their permissible levels of exposure have been reduced to 10 parts per billion (ppb). A hydrazine spill remediation process, to be developed, should not only destroy the propellant fuel but also should not generate other hazardous materials. An in-situ processing method involving direct application of the treatment reagent or process to the spill is preferred.

Currently, a small hydrazine spill, occurring at launch facilities, is washed down with water. The diluted water is treated with an oxidizing agent such as sodium hypochlorite or alternatively, the hydrazine containing water is transported to a hazardous waste facility for incineration. The former treatment method with UDMH is unsatisfactory in that a strong carcinogen, n-Nitrosodimethylamine, is generated. In addition, the hypochlorite oxidation of both UDMH and MMH yields volatile halogenated hydrocarbons, which are priority pollutants. In the case of a spill on soil, the contaminated material is transported for disposal at an incineration facility.

An accident involving a transport trailer may spill four to five thousand gallons of the hydrazine fuel, whereas a catastrophic failure of a fuel storage vessel at a launch facility may release twenty thousand gallons or more of the propellant. A rail car derailment resulting in a hydrazine (i.e., commercial use) release occurred in Southern California several years ago.

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A major spill of a hydrazine transport trailer could potentially result in legal action amounting to millions of dollars. Additionally, minor hydrazine spills resulting from leaks or other causes are not unusual during space launch operations.

These spills, which can result in evacuations and expensive launch delays, are washed down into the waste fuel tank for later disposal. A greater concern is a major accidental spill of a hydrazine transport trailer, occurring off-site during shipment of the propellant over the public highways. Although such an incident has not occurred to date, a treatment/disposal process should be developed and be available when needed. An environmentally conscious, inexpensive method for the complete conversion of the spilled hydrazine into innocuous materials is needed. This treatment process may entail chemical reactions, bioremediation, or other methods such as pyrolysis, photolysis, or catalysis.

Hydrazine group compounds, including hydrazine, monomethylhydrazine (MMH), and 1,1-dimethylhydrazine (UDMH), are widely used as fuels (e.g., in rocket propulsion systems and fighter jets), corrosion inhibitors (e.g., nuclear industry), catalysts, emulsifiers, or dyes. Hydrazine is typically utilized as a monopropellant in rocket propulsion applications because it can readily ignite when placed in contact with noble metal catalysts. Hydrazine is particularly popular with satellite companies because hydrazine, when used as a monopropellant, saves space, complexity and weight. Hydrazine and hydrazine-based compounds can also function as precursors in the synthesis of a number of drugs, polymers, plasticizers and pesticides. As indicated above, however, hydrazine is also extremely toxic and dangerous. Note that as utilized herein, the term "hydrazine" is generally analogous to the chemical formula N_2H_4 , while the term monomethylhydrazine (MMH) is generally analogous to the chemical formula CH_3NHNH_2 . Additionally, the term dimethylhydrazine (UDMH) can be referred to by the chemical formula $(CH_3)_2NNH_2$.

The U.S. Occupational Safety and Health Administration (OSHA), for example, requires the prevention of exposure to hydrazine and its derivatives at concentrations greater than one part per million (1.3 mg/m^3). Hydrazine and hydrazine derivatives are readily combustible reducing agents that react violently with oxidizing agents and thus present a serious safety hazard. Hydrazine and hydrazine derivatives are well known components of liquid rocket fuels in conjunction with an oxidizing agent such as dinitrogen tetroxide. Thus, at facilities where liquid-fueled rockets are prepared for flight, there is a particular need to provide reliable and sensitive methods and systems for decontaminating objects, such as fighter jets and maintenance equipment thereof, and exposed environments which can become contaminated with hydrazine. Ideally, such hydrazine remediation methods and systems should also have a limited, if negligible effect on the environment.

Many reactions of hydrazine with dicarbonyl compounds are known. For example, Gerd Kaupp and Jens Schmeyerers have investigated hydrazine reactivity, as reported in "Solid-State Reactivity of the Hydrazine-Hydroquinone Complex," J. Phys. Org. Chem 2000, 13: pp. 388-394, which is incorporated herein by reference. Kaupp and Schmeyerers investigated the solid-state reactivities of the hydrazine-hydroquinone 1:1 complex and of hydrazine hydrochloride with solid aldehydes, ketones, carboxylic acids, thiohydantoin and 4-nitrophenyl isothiocyanate. Kaupp and Schmeyerers reported that only the hydrazine complex provides quantitative additions, condensations, ring openings and ring closures. The solid-state mechanisms were investigated

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by atomic force microscopy (AFM) and far-reaching anisotropic molecular movements were correlated with the crystal packing, both on the hydrazine complex surface and on the surface of two benzaldehydes. Based on this research Kaupp and Schmeyers concluded that the hydrazine can move into the aldehyde crystals for chemical reaction without melting. Kaupp and Schmeyers also reported that characteristic surface features could be created by common phase rebuilding and phase transformation on both the hydrazine-donating and -accepting crystals.

The present inventors have examined compounds that will react with hydrazine rapidly and quantitatively. The present inventors have investigated several compound classes in order to tailor these derivatives of hydrazine for facile detection (i.e., to required levels) by current analytical methods.

Decontamination methods and systems can be separated into three major categories: physical removal, chemical inactivation, or a combination of both physical and chemical means. Wiping, sweeping, scraping, blowing, vacuuming, rinsing with water, and steam cleaning are all examples of physical methods for the removal of contaminants. In many cases, physical removal of gross contamination is an initial step in decontamination and remediation thereof. Physical removal of gross contamination usually is not sufficient to reduce contaminant concentrations to background levels. In most cases, physical removal is followed by a wash and rinse process using cleaning solutions. These cleaning solutions often dissolve contaminants and keep them in a solution until they can be rinsed away. Rinsing removes contaminants from an affected object or area through the dual process of dilution and solubilization. Multiple rinses with clean water can remove more contaminants than a single rinse.

Despite use of present cleaning solutions and rinsing procedures, contaminants generally still persist after remediation, although in a diluted form, and can be relocated to areas surrounding the object or area targeted for decontamination. Such is the case where hydrazine is diluted and allowed to run off along a surface (e.g., earth or pavement) away from the decontamination zone, or worse is absorbed into the earth and into water aquifers.

More effective methods and systems are needed for remediating hydrazine from contaminated objects, solutions, and areas. The present inventors recognize this need and have invented method of and systems for hydrazine remediation.

BRIEF SUMMARY OF THE INVENTION

The following summary of the invention is provided to facilitate an understanding of some of the innovative features unique to the present invention, and is not intended to be a full description. A full appreciation of the various aspects of the invention can be gained by taking the entire specification, claims, drawings, and abstract as a whole.

It is therefore one aspect of the present invention to provide improved remediation methods and systems.

It is therefore another aspect of the present invention to provide methods and systems for remediating hydrazine from hydrazine contaminated objects and areas thereof.

It is yet an additional aspect of the present invention to provide an aqueous solution prepared from a dicarbonyl-compound.

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It is yet an additional aspect of the present invention to provide a cleaning solution that includes a dicarbonyl-compound for converting hydrazine to a stable organic compound.

It is still an additional aspect of the present invention to treat a stable organic compound produced as a result of a reaction between a dicarbonyl-compound and a hydrazine with a metal catalyst and hydrogen to produce glutamine or a derivative thereof.

The above and other aspects of the invention can be achieved as will now be described. Methods and systems for remediating hydrazine from hydrazine-contaminated objects (including areas) are disclosed herein. Initially, an aqueous solution comprising a dicarbonyl-compound can be prepared. Such a dicarbonyl-compound can be, for example, 2-ketoglutaric acid. (Note that the term "dicarbonyl-compound" as utilized herein generally refers to a dialdehyde, diketone, aldehyde-ketone, aldehyde-add, aldehyde-ester, keto-acid and/or a keto-ester.) The aqueous solution can then be applied to an object contaminated with a hydrazine group compound, such that the hydrazine group compound is converted to a stable organic compound as a result of a reaction of the dicarbonyl-compound and hydrazine group compound in order to remediate the hydrazine group compound from the object. Such a hydrazine group compound can be, for example, hydrazine (Hz), monomethylhydrazine (MMH), or 1,1 dimethylhydrazine (UDMH).

The solution, which may be aqueous, can be applied to the object contaminated with the hydrazine group compound following an initial attempt at a physical removal (e.g., wiping, sweeping, scraping, blowing, vacuuming, rinsing with water, steam cleaning, etc.) of the hydrazine group compound from the area, object or solution. Alternatively, the aqueous solution can be applied directly to the object, thereby skipping this physical removal step. The solution can be prepared in the form of a cleaning solution. Application of such an aqueous or cleaning solution to the object can occur by rinsing the object with the solution. Finally, the stable organic compound produced as a result of the reaction between the dicarbonyl-compound and hydrazine group compound can then be treated by microbiological degradation or with a metal catalyst and hydrogen to produce glutamine or a derivative thereof. The glutamine can then be permitted to undergo microbiological degradation thereof.

BRIEF DESCRIPTION OF THE DRAWINGS


The accompanying figures, in which like reference numerals refer to identical or functionally-similar elements throughout the separate views and which are incorporated in and form part of the specification, further illustrate the present invention and, together with the detailed description of the invention, serve to explain the principles of the present invention.

FIG. 1 illustrates a schematic diagram depicting a reaction between a dicarbonyl-compound and a complex of hydrazine;

FIG. 2 depicts a schematic diagram illustrating a production of glutamine;

FIG. 3 illustrates a schematic diagram depicting a reaction of 2-ketoglutaric acid, which provides a near quantitative conversion of hydrazine to a 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid, in accordance with a preferred embodiment of the present invention;

FIG. 4 depicts a schematic diagram illustrating the reaction of MMH and UDMH with 2-ketoglutaric acid followed

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by hydrogenation, in accordance with a preferred embodiment of the present invention;

FIG. 5 illustrates a high-level flow chart of operations illustrating logical operational steps, which can be implemented in accordance with a preferred embodiment of the present invention;

FIG. 6 depicts a high-level flow chart of operations illustrating logical operational steps, which can be implemented in accordance with a preferred embodiment of the present invention; and

FIG. 7 illustrates a plot of experimental data, which can be collected in accordance with an alternative embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The particular values and configurations discussed in these non-limiting examples can be varied and are cited merely to illustrate an embodiment of the present invention and are not intended to limit the scope of the invention.

FIG. 1 illustrates a schematic diagram 100 depicting a reaction between a dicarbonyl-compound and a complex of hydrazine. Two cases 102 and 104 are illustrated in FIG. 1. In each case, the solid compounds were ball milled at room temperature in a ratio of 2:1 (dicarbonyl-compound to hydrazine complex) and a near quantitative yield was obtained. The 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid formed from the reaction of 2-ketoglutaric acid and the hydrazine complex comprises a high melting solid (i.e., melting point within a range of approximately 106° C.–198° C.).

FIG. 2 depicts a schematic diagram 200 depicting the treatment of hydrazine waste to glutamine or a derivative thereof, in accordance with a preferred embodiment of the present invention. The hydrogenization of pyridazine using 5% Pd/C can provide glutamine in a 45% yield. Although this pyridazine is not easily biodegraded, the present inventors believe that glutamine can be utilized as a plant nutrient or that it is easily biodegradable. Glutamine can be specifically utilized as a source of energy and for nucleotide synthesis by all rapidly dividing cells. Thus, rather than acting as an environmental hazard, glutamine or a derivative can actually benefit plants exposed to it during a hydrazine remediation process, as described herein.

FIG. 3 illustrates a schematic diagram 300 depicting a reaction of 2-ketoglutaric acid, which provides a near quantitative conversion of hydrazine to a 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid, a preferred embodiment of the present invention. In general, the chemical transformation depicted in schematic diagram 300 of FIG. 3 allows for the removal of hydrazine from aqueous solutions generated by the decontamination processes described herein. The reaction with concentrated hydrazine also can provide the desired product with some evolution of heat. The low solubility of the compound in water allows for the separation of most of this adduct by a simple filtration.

The MSDS for 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid does not list any known acute toxicities and thus it should be a nonhazardous waste. However the ideal situation would be to find a method for the safe destruction or remediation of the 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid. The use of microbes (e.g., a pseudomonas species found in the soil) as a method for the metabolism of a nitrogen-nitrogen bond can thus be implemented, in accordance with the methods and systems described herein. After about ten minutes thereafter, a white precipitate can be formed, which is generally characterized by Nuclear Magnetic Resonance to be the expected product, 6-oxo-1,4,5,6-

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tetrahydro-pyridazine-3-carbonic acid. The reaction generally appears to be a quantitative reaction with the aqueous hydrazine.


FIG. 4 depicts a schematic diagram 400 illustrating the reaction of MMH and UDMH with 2-ketoglutaric acid followed by hydrogenation, in accordance with a preferred embodiment of the present invention. The schematic diagram 400 depicted in FIG. 4 can be implemented by adding a sample of the hydrazine derivative to a slight excess of an aqueous solution of 2-ketoglutaric acid. Note that the solution described herein (i.e., which includes a dicarbonyl-compound) can be prepared as aqueous solution or a non-aqueous solution, depending on particular desired applications. Thus, the use of an aqueous solution is not considered a limiting feature of the present invention. Rather the use of an aqueous solution represents merely one possible embodiment of the present invention. Non-aqueous solutions represent another possible embodiment of the present invention.

FIG. 5 illustrates a high-level flow chart 500 of operational steps, which can be implemented in accordance with a preferred embodiment of the present invention. As illustrated at block 502, a solution can be prepared that includes, as indicated at next at block 504, a dicarbonyl-compound. Such a solution can be prepared in the form of a cleaning solution. The solution can be an aqueous solution or a non-aqueous solution. An example of a dicarbonyl-compound that can be utilized in accordance with the methods and systems of the present invention is a keto-acid, such as a 2-ketoglutaric acid. Once the solution has been prepared, it can be provided for utilization in hydrazine remediation.

As indicated next at block 506, the solution as provided via processing of the operations described at blocks 502 and 504 can be applied to an object contaminated with a hydrazine group compound. Application can occur, for example, through a rinsing of the hydrazine contaminated object with the solution that includes the dicarbonyl-compound. Examples of hydrazine group compounds that may contaminate an object or area thereof can include simply hydrazine, MMH, or UDMH.

It can be appreciated by those skilled in the art that the application of the dicarbonyl compound solution to the hydrazine contaminated object and/or area (e.g., a hydrazine spill) thereof can take place following an initial attempt at a physical removal of the hydrazine group compound from the object or area thereof. As indicated previously, wiping, sweeping, scraping, blowing, vacuuming, rinsing with water, and steam cleaning are all examples of physical methods for the removal of contaminants. Such physical removal techniques can thus occur in tandem with the application of the dicarbonyl-compound solution described herein.

A reaction can then occur, as illustrated at block 508 between the hydrazine group compound and the dicarbonyl-compound. As a result of this reaction, the hydrazine group compound is converted to a stable organic compound, as indicated at block 510, in order to remediate the hydrazine group compound from the object. Thus, based on the foregoing it can be appreciated that the present invention allows for the use of a solution of a dicarbonyl-compound (e.g. 2-ketoglutaric acid) for the treatment of hydrazine waste. Prior art solutions for the treatment of hydrazine generally involve solubilization and dilution processes. The hydrazine remediation methods and systems described herein do not only involve solubilization and dilution. Rather, the present invention involves a conversion of hydrazine to a stable organic compound. Such a conversion can occur after application of the dicarbonyl-compound solution through the use of solubilization and dilution processes, among others. Note that the step of treating a stable organic compound with a

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metal catalyst and hydrogen to produce glutamine, can also include the step of producing a derivative of glutamine, rather than simply glutamine.

FIG. 6 depicts a high-level flow chart 600 of operations illustrating logical operational steps, which can be implemented in accordance with a preferred embodiment of the present invention. Once the stable organic compound has been created as a result of the reaction between hydrazine and the dicarbonyl-compound, the stable organic compound can be treated with a metal catalyst and hydrogen to produce glutamine and/or a derivative thereof.

Thus, as indicated at block 602, treatment of the stable organic compound can be initiated. The compound (or solid material formed thereof) can be isolated as indicated at block 603. A decision can be made, as indicated at block 604, to determine whether or not the stable organic, should be treated at another location, or treated directly, as indicated by processes described at blocks 606 to 610. If it is determined to isolate the stable organic compound for treatment at another location, then the operation indicated at block 610 can be processed elsewhere. As indicated at block 610, any remaining material (i.e., the stable organic compound) can simply be digested via soil microbes.

If necessary, however, the stable organic compound can be treated with a metal catalyst and hydrogen as illustrated at block 606, which follows decision block 604. As depicted at block 606, a reaction can occur between the metal catalyst and hydrogen and the stable organic compound. As a result of this reaction, glutamine or a glutamine derivative can be produced, as depicted at block 608. Finally, as illustrated at block 610 complete digestion with soil microbes can occur. For example, the reaction of hydrazine with a 2-ketoglutaric acid, followed by hydrogenation, can yield glutamic acid, a compound, which has been utilized to enhance fertilizer use.

A system for remediating hydrazine in accordance with the present invention thus generally includes a solution that can be formed from a dicarbonyl-compound, and an application mechanism for applying the solution to an object or area (e.g., a spill) contaminated with a hydrazine group compound. A dicarbonyl-compound can be implemented as a solution (e.g. an aqueous solution), which can then be applied to an object or area contaminated with a hydrazine group compound. Such a hydrazine group compound can include at least one of the following: hydrazine (Hz), monomethylhydrazine (MMH), and 1,1 dimethylhydrazine (UDMH). The application mechanism itself can be implemented as a rinsing mechanism for rinsing the object contaminated with the hydrazine group compound with the solution. Such a rinsing mechanism can be, for example, a hose or other fluid delivery device and/or system. The application mechanism can also be implemented in the form of objects or devices such as sponges, pads, spray bottles, and so forth. A metal catalyst and hydrogen can thus be applied to the contaminated objects with the application mechanism to produce glutamine thereof.

FIG. 7 illustrates a plot 700 of experimental data, which can be collected in accordance with an alternative embodiment of the present invention. Note that a graph 704 is associated with chart 702, which depicts such experimental data. Note that the experimental techniques utilized to collect the data depicted in FIG. 7 represent merely one possible embodiment of the present invention. Those skilled in the art can appreciate that many other embodiments can be implemented. An insulated reaction vessel can be utilized to insure that heat evolution will not be underestimated. A 1-cup Styrofoam™ cup equipped with stir bar and thermometer, 75 mL of 2-ketoglutaric acid solution can be added and stirred a few minutes before the addition of a 1.1 eq of

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hydrazine monohydrate. The temperature can be monitored at 30 sec to 1-minute intervals for 15 minutes. After about 45 seconds, seed crystals of 6-oxo-1,4,5,6-tetrahydropyridazin-3-carboxylic acid can be added to the solution; otherwise two exotherms can be observed (i.e., one large temperature rise immediately and second smaller one after about 10 minutes associated with the heat of crystallization). Initial temperatures can be about 18° C., and the highest final temperature can be approximately 84° C., although the some boiling occurred in the mixing zone as the hydrazine can be added to the 41.5% 2-ketoglutarate solution.

Hydrazine monohydrate (98%), deuterium oxide and dimehtylsulfoxide-d₆ can be utilized, along with 6-oxo-1,4,5,6-tetrahydropyridazin-3-carboxylic acid (97%) and 2-ketoglutaric acid (98%) to produce the following results. The reaction of solid 2-ketoglutaric acid with hydrazine monohydrate can generally be produced as follows: A 2-ketoglutarate (450 mg) can be combined with hydrazine monohydrate (70 µL), which produces heat immediately. Extraction of the reaction residue with water may only partially dissolved the solid, and the solution provided an NMR spectrum consistent with unreacted starting material and the expected product. The remaining solid can be dissolved in a mixture of MeOH, chloroform and DMSO, and can possess NMR spectra consistent with the expected product.

Note that a product from one of the aforementioned reactions can be derived with N,N-bis(trimethylsilyl)trifluoroacetamide at room temperature and analyzed by both EI and CI mass spectrometry. In the EI spectrum, several chromatographic peaks can be observed with the largest corresponding to the 6-oxo-1,4,5,6-tetrahydropyridazin-3-carboxylic acid. One peak can be viewed for in a CI chromatogram with a mass spectrum dominated by 287 m/z (M+1). The mass balance of the product can be high and the melting point low, presumably owing to inclusion of the hydrazinium salt of the product. Addition of a 10% equivalent of 2-ketoglutaric acid to consume excess hydrazine, and recrystallization from hot water can afford a material with the same melting point as the standard material, 194–196° C. NMR chemical shifts can vary with concentration and pH, and are generally identical to the standard material: H (δ, D₂O, MeOH ref. 3.30 ppm, 300 MHz) 2.56 (2H, t, J_{H-H} 8.9 Hz), and 2.85 (2H, t, 8.9 Hz) ppm; ¹³C (δ, D₂O, MeOH set to 49.0 ppm, 75 MHz) 20.6, 24.9, 146.0, 166.1, and 170.9 ppm.

The present invention offers a number of advantages. The removal of hydrazine according to the methods and systems described herein will allow for the remediation of hydrazine to useful by-products or biodegradable forms, which not only provide environmental benefits, but also reduces the cost of hydrazine waste disposal. The methods and systems described here can be utilized at airports, military facilities, and rocket launches and space vehicle-landing pads (e.g., the Space Shuttle). In particular, the present invention can also find use in orbiting facilities such as the International Space Station in which hydrazine exposure can be problematic. The present invention has particularly useful applications to wash water cleanup and spill abatement.

The embodiments and examples set forth herein are presented to best explain the present invention and its practical application and to thereby enable those skilled in the art to make and utilize the invention. Those skilled in the art, however, will recognize that the foregoing description and examples have been presented for the purpose of illustration and example only. Other variations and modifications of the present invention will be apparent to those of skill in the art, and it is the intent of the appended claims that

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such variations and modifications be covered. The description as set forth is not intended to be exhaustive or to limit the scope of the invention. Many modifications and variations are possible in light of the above teaching without departing from the spirit and scope of the following claims. It is contemplated that the use of the present invention can involve components having different characteristics. It is intended that the scope of the present invention be defined by the claims appended hereto, giving full cognizance to equivalents in all respects.

The invention claimed is:

1. A method for neutralizing harmful effects of hydrazine contamination, said method comprising the steps of:

providing an aqueous solution comprising a 2-ketoglutaric acid, said solution adapted for application to hydrazine contaminated equipment and/or ground surfaces; and

applying said solution to equipment and/or ground surfaces contaminated with a hydrazine group compound, wherein said hydrazine group compound is converted to a stable organic compound as a result of a reaction between said solution comprising said 2-ketoglutaric acid and said hydrazine group compound.

2. The method of claim 1 wherein the step of applying said solution to an equipment and/or ground surfaces contaminated with a hydrazine group compound, further comprises the step of:

applying said aqueous solution to said object contaminated with said hydrazine group compound following physical removal of debris also contaminated with said hydrazine group compound from said equipment and/or ground surfaces.

3. The method of claim 1 wherein the step of applying said aqueous solution to an equipment and/or ground surfaces contaminated with a hydrazine group compound, further comprises the step of:

using an application mechanism to rinse said equipment and/or ground surfaces contaminated with said hydrazine group compound with said aqueous solution.

4. The method of claim 1 further comprising the step of: treating said stable organic compound with a metal catalyst and hydrogen to produce glutamine thereof, wherein said hydrazine group compound is converted to a stable organic compound as a result of a reaction of said 2-ketoglutaric acid and hydrazine group compound.

5. The method of claim 1 wherein said hydrazine group compound comprises monomethylhydrazine (MMH).

6. The method of claim 1 wherein said hydrazine group compound comprises 1,1 dimethylhydrazine (UDMH).

7. The method of claim 1 wherein said aqueous solution is a cleaning solution.

8. A method for treating hydrazine contaminated equipment and/or ground surfaces comprising the steps of:

providing a cleaning solution that includes 2-ketoglutaric acid; and

rinsing at least one of equipment or ground surfaces contaminated by a hydrazine group compound with said cleaning solution.

9. A method using a dicarbonyl-compound for decontaminating equipment and/or ground surfaces accidentally contaminated in an operational environment or during an operational activity with a hydrazine group compound, said method comprising the steps of:

providing an application mechanism adapted to manage use of an aqueous cleaning solution said aqueous cleaning solution comprising 2-ketoglutaric acid; and

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applying said aqueous cleaning solution to equipment and/or ground surfaces contaminated with a hydrazine group compound, wherein said hydrazine group compound is converted to a stable organic compound as a result of a chemical reaction between said aqueous solution and said hydrazine group compound.

10. A system for treating hydrazine-contaminated equipment or groundsurfaces, said system comprising:

an aqueous solution comprising a 2-ketoglutaric acid; and an application mechanism for enabling a user to manage the application of said aqueous solution to equipment or ground surfaces accidentally contaminated with a hydrazine group compound, wherein said hydrazine group compound is converted to a stable organic compound as a result of a reaction between said aqueous solution comprising said dicarbonyl-compound and said hydrazine group compound.

11. The system of claim 10 wherein said hydrazine group compound comprises includes at least one of the following: hydrazine (Hz), monomethylhydrazine (MMH), and 1,1 dimethylhydrazine (UDMH).

12. The system of claim 10 wherein said application mechanism further comprises:

a rinsing mechanism for rinsing said object contaminated with said hydrazine group compound with said aqueous solution.

13. The system of claim 10, further comprising a metal catalyst and hydrogen, said metal catalyst and hydrogen is applied to said contaminated objects with said application mechanism to produce glutamine thereof.

14. The system of claim 13 wherein said hydrazine group compound comprises at least one of the following: hydrazine (Hz), monomethylhydrazine (MMH), and 1,1 dimethylhydrazine (UDMH).

15. The system of claim 10 wherein said hydrazine group compound comprises hydrazine.

16. The system of claim 1 wherein said hydrazine group compound comprises monomethylhydrazine (MMH).

17. The method of claim 10 wherein said hydrazine group compound comprises 1,1 dimethylhydrazine (UDMH).

18. The system of claim 10 wherein said aqueous solution comprises a cleaning solution.

19. A system for remediating equipment and/or ground surfaces contaminated with hydrazine, said system comprising:

a cleaning solution comprising a 2-ketoglutaric acid; a metal catalyst and hydrogen; and

a rinsing mechanism for rinsing said equipment and/or ground surfaces contaminated with a hydrazine group compound with said cleaning solution, said metal catalyst and said hydrogen.

20. A system for decontaminating equipment and/or ground surfaces contaminated with a hydrazine group compound, said system comprising:

an aqueous solution managed by an application mechanism and comprising 2-ketoglutaric acid; and

an application mechanism for enabling a user in the application of said aqueous solution to equipment and/or ground surfaces accidentally contaminated with a hydrazine group compound, wherein said hydrazine group compound is converted to a stable organic compound as a result of a reaction between said aqueous solution comprising said 2-ketoglutaric acid and said hydrazine group compound.

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